SUPPLEMENTARY MATERIAL

Two new Oleanane Triterpenoid Saponins from *Elsholtzia* bodinieri

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Two new oleanane triterpenoid saponins, bodiniosides Q (1) and R (2), along with five known saponins, niga-ichigoside F1 (3), 3-*O*-[β -D-glucopyranosyl]-28-*O*-[α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranosyl] arjunolic acid (4), asiaticoside E (5), sericoside (6), bodinioside E (7), were isolated from the aerial parts of Elsholtzia bodinieri. The structures of 1 and 2 were characterized by spectroscopic techniques and chemical evidence as $3-O-\beta$ -Dxylopyranosyl- 2α , 23-dihydroxy-olean-12-en-28-oicacid 28-O- α -L-rhamnopyranosyl- $(1\rightarrow 2)$ - β -D-glucopyranoside (1) and 3-O- β -D-xylopyranosyl-2 α ,23-dihydroxyolean-12-en-28-oicacid 28-*O*-[β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl- $(1\rightarrow 2)$]- β -D-glucopyranoside (2). Compounds 1, 3, and 5 exhibited weak anti-influenza activity against strain A/WSN/33/2009 (H1N1), with inhibition rate of 11.63%, 17.01% and 16.98%, respectively.

Key words: *Elsholtzia bodinieri*; oleanane triterpenoid; saponins; anti-icnfluenza virus activities

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| Position | 1 | | Position | 2 | | |
|----------|----------------|----------------------------------|----------|----------------|----------------------------------|--|
| | δ mult. | δ mult. (<i>J</i> in Hz) | | δ mult. | δ mult. (<i>J</i> in Hz) | |
| 1 | 47.9 | 1.17 (overlap) | 1 | 47.0 | 1.17 (overlap) | |
| 2 | 66.8 | 4.21 (m) | 2 | 66.7 | 4.12 (m) | |
| 3 | 88.2 | 3.30 (m) | 3 | 88.2 | 3.70 (m) | |
| 4 | 41.9 | | 4 | 41.8 | | |
| 5 | 47.2 | 0.93 (m) | 5 | 47.3 | 1.26 (m) | |
| 6 | 18.6 | 1.52 (m) | 6 | 18.6 | 1.67 (m) | |
| 7 | 33.0 | 1.36 (m) | 7 | 32.9 | 1.85 (m) | |
| 8 | 41.9 | | 8 | 41.8 | | |
| 9 | 48.1 | 1.82 (m) | 9 | 48.1 | 1.69 (m) | |
| 10 | 37.7 | | 10 | 37.8 | | |
| 11 | 23.9 | 1.98 (m) | 11 | 23.6 | 1.92 (m) | |
| 12 | 122.4 | 5.42 (br. s) | 12 | 123.2 | 5.39 (br. s) | |
| 13 | 144.1 | | 13 | 144.0 | | |
| 14 | 44.6 | | 14 | 44.6 | | |
| 15 | 28.5 | 2.13 (m) | 15 | 28.4 | 2.32 (m) | |
| 16 | 23.3 | 2.33 (m) | 16 | 23.3 | 2.03 (m) | |
| 17 | 48.1 | | 17 | 48.0 | | |
| 18 | 42.2 | 3.08 (d, <i>J</i> = 13.6) | 18 | 42.2 | 3.09 (d, <i>J</i> =13.5) | |
| 19 | 46.2 | 1.70 (m) | 19 | 44.6 | 1.66 (m) | |
| 20 | 30.6 | | 20 | 30.6 | | |
| 21 | 33.9 | 1.31 (m) | 21 | 33.8 | 1.38 (m) | |
| 22 | 33.0 | 1.66 (m) | 22 | 32.9 | 1.65 (m) | |
| 23 | 63.4 | 4.34 (m) | 23 | 66.7 | 4.40 (m) | |
| 24 | 14.6 | 0.96 (s) | 24 | 14.6 | 0.92 (s) | |
| 25 | 17.4 | 1.03 (s) | 25 | 17.4 | 1.00 (s) | |
| 26 | 17.4 | 1.10 (s) | 26 | 17.5 | 1.08 (s) | |
| 27 | 30.6 | 1.15 (s) | 27 | 30.6 | 1.13 (s) | |
| 28 | 176.3 | | 28 | 176.3 | | |
| 29 | 33.0 | 0.83 (s) | 29 | 32.9 | 0.81 (s) | |
| 30 | 25.7 | 0.78 (s) | 30 | 25.8 | 0.78 (s) | |
| 3-Xyl | | | | | | |
| 1 | 106.3 | 5.02 (d, <i>J</i> = 7.3) | 1 | 107.0 | 5.16 (d, <i>J</i> = 7.3) | |
| | | | | | | |

Table S2. ¹H and ¹³C NMR data for compounds **1** and **2** in pyridine- d_5 (150/600 MHz)

| 2 | 75.6 | 4.04 (overlap) | 2 | 75.3 | 3.97 (overlap) |
|---------------------|-------|---------------------------------|---|-------|---------------------------------|
| 3 | 78.5 | 4.14 (overlap) | 3 | 78.6 | 4.01 (overlap) |
| 4 | 71.2 | 4.21 (overlap) | 4 | 71.6 | 4.29 (overlap) |
| 5 | 67.2 | 4.33 (overlap) | 5 | 67.2 | 4.40 (overlap) |
| | | 3.61 (overlap) | | | 3.54 (overlap) |
| 28- <i>O</i> -sugar | | | | | |
| Glc | | | | | |
| 1 | 94.8 | 6.19 (d, <i>J</i> = 8.1) | 1 | 94.6 | 6.16 (d, <i>J</i> = 8.2) |
| 2 | 75.3 | 4.04 (t, <i>J</i> = 8.6) | 2 | 76.3 | 4.11 (t, <i>J</i> = 7.8) |
| 3 | 79.7 | 4.20 (t, <i>J</i> = 8.2) | 3 | 79.2 | 4.41 (t, <i>J</i> = 8.3) |
| 4 | 70.7 | 4.18 (t, <i>J</i> = 9.0) | 4 | 71.1 | 4.61 (t, <i>J</i> = 9.5) |
| 5 | 78.9 | 4.17 (overlap) | 5 | 78.8 | 4.49 (overlap) |
| 5 | 61.9 | 4.49 (overlap) | 6 | 62.8 | 4.38 (dd, <i>J</i> = 11.7, 5.3) |
| | | 4.41 (dd, <i>J</i> = 12.1, 2.0) | | | 4.30 (dd, <i>J</i> = 11.7, 2.2) |
| Rha | | | | | |
| 1 | 101.4 | 6.11 (br. s) | 1 | 101.3 | 6.46 (br. s) |
| 2 | 72.2 | 4.40 (dd, <i>J</i> = 3.2, 1.5) | 2 | 71.6 | 4.21 (overlap) |
| 3 | 72.4 | 4.56 (overlap) | 3 | 72.4 | 4.73 (dd, <i>J</i> = 9.1, 3.2) |
| 4 | 73.8 | 4.42 (t, <i>J</i> = 9.0) | 4 | 85.4 | 3.98 (t, <i>J</i> = 9.1) |
| 5 | 69.7 | 4.55 (overlap) | 5 | 70.7 | 4.25 (overlap) |
| 6 | 18.6 | 1.75 (d, <i>J</i> = 6.1) | 6 | 18.2 | 1.86 (d, <i>J</i> = 6.0) |
| Glc' | | | | | |
| | | | 1 | 106.3 | 5.03 (d, <i>J</i> = 7.3) |
| | | | 2 | 76.5 | 4.02 (dd, <i>J</i> = 8.5, 7.3) |
| | | | 3 | 78.6 | 3.33 (t, <i>J</i> = 8.5) |
| | | | 4 | 71.1 | 3.09 (t, <i>J</i> = 9.4) |
| | | | 5 | 78.3 | 3.07 (overlap) |
| | | | 6 | 63.5 | 3.85 (dd, <i>J</i> = 12.1, 5.2) |
| | | | | | 3.55 (dd, <i>J</i> = 12.1, 2.1) |



Figure S1. Key HMBC correlation of compound $\mathbf{1}$



Figure S2. Key HMBC correlation of compound 2



Figure S3. ¹H NMR spectrum of compound $1(600 \text{ MHz}, \text{ pyridine-}d_5)$



Figure S4. ¹³C NMR spectrum of compound $1(150 \text{ MHz}, \text{ pyridine-}d_5)$



Figure S4. HSQC spectrum of compound 1







Figure S8. HRESIMS spectrum of compound 1



Figure S9. FABMS spectrum of compound 1



Figure S10. ¹H NMR spectrum of compound **2**(600 MHz, pyridine-*d*₅)



Figure S11. ¹³C NMR spectrum of compound $2(150 \text{ MHz}, \text{ pyridine-}d_5)$



Figure S6. HSQC spectrum of compound 2



Figure S13. HMBC spectrum of compound ${f 2}$









Figure S8. HRESIMS spectrum of compound 2



Figure S9. FABMS spectrum of compound ${\bf 2}$