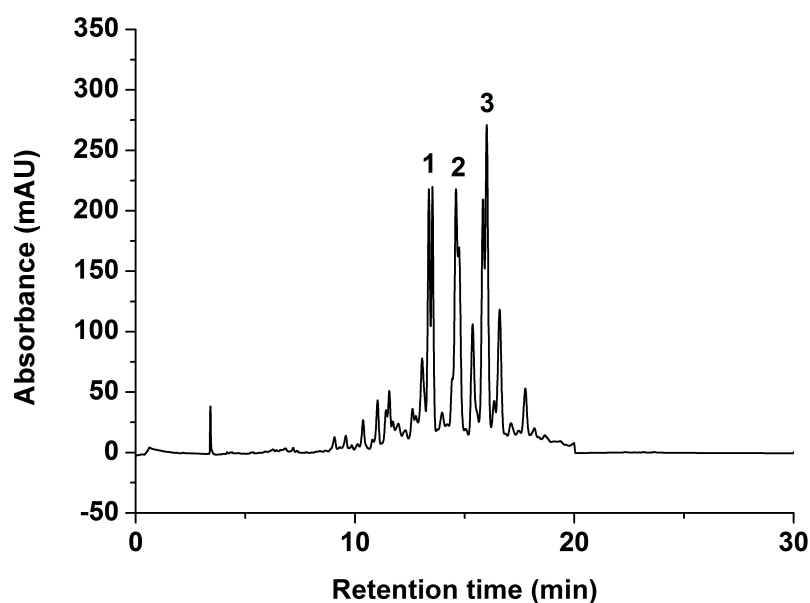


## Supplementary materials

Using high performance liquid chromatography-mass spectrum (HPLC-MS, Agilent 1290-6460 HPLC System, Agilent Technologies, Inc., CA, USA) and nuclear magnetic resonance (NMR, 400-MR DD2 spectrometer, Agilent Technologies Inc., CA, USA), the main active compounds of LRE were identified to be Ligurobustoside B (LGB), Ligurobustoside N (LGN) and Ligupurpurososide J (LPJ), respectively.



**Figure S1. The results of High performance liquid chromatography (HPLC)**

Methanol (A) and deionized water with 0.1% formic acid (B) were used as mobile phase. Gradient elution was set as: 0-10 min, 0-50% A; 10-15 min, 50-60% A; 15-20 min, 60-70% A; 20-25 min, 70-80% A; 25-30 min, 80-90% A; 35-40 min, 90-100% A; 45-60 min, 100% A. The analytical conditions were the following: column temperature, 25 °C; flow rate, 1 mL/min; injection volume, 20  $\mu$ L (the concentration of LRE: 10  $\mu$ g/ $\mu$ L), and detection, 320 nm. The mass spectra were performed using TSQ Quantum Ultra (Thermo, USA) with an electrospray source operating in negative ion mode and a mass spectrum scanning range from 50 to 1200 m/z.

## 1. The results of mass spectrum (MS) and nuclear magnetic resonance (NMR)

### Compound 1: Ligurobustoside B (LGB)

ESI-MS m/z: 623 [M-H]<sup>-</sup>, Molecular formula: C<sub>31</sub>H<sub>44</sub>O<sub>13</sub>

<sup>1</sup>H-NMR (CD<sub>3</sub>OD, 600 MHz) δ: 7.62 (1H, d, *J*=15.9 Hz, H-7'''), 7.08 (1H, d, *J*=2.3 Hz, H-2'''), 6.94 (1H, dd, *J*=8.3, 2.1 Hz, H-5'''), 6.82 (1H, d, *J*=8.1 Hz, H-6'''), 6.23 (1H, d, *J*=15.7 Hz, H-8'''), 5.38 (1H, t, *J*=7.1 Hz, H-2), 5.06 (1H, t, *J*=6.5 Hz, H-6), 4.39 (1H, dd, *J*=12.1, 7.3 Hz, H-1a), 4.22 (1H, dd, *J*=11.5, 7.3 Hz, H-1b), 2.15 (2H, t, *J*=6.5 Hz, H-5), 1.97 (2H, t, *J*=7.5 Hz, H-4), 1.74 (6H, s, H-8, 10), 1.58 (3H, s, H-9)

<sup>13</sup>C-NMR (CD<sub>3</sub>OD, 150 MHz) δ: 168.6 (C=O), 150.2 (C-4'''), 148.2 (C-8'''), 147.1 (C-3'''), 141.9 (C-3), 133.6 (C-7), 127.4 (C-1'''), 125.7 (C-6), 123.5 (C-6'''), 121.3 (C-2), 116.8 (C-5'''), 115.1 (C-2'''), 114.6 (C-7'''), 103.4 (C-1'), 102.3 (C-1''), 82.1 (C-3'), 76.5 (C-2', 5'), 73.6 (C-4''), 72.3 (C-2''), 71.9 (C-3''), 70.6 (C-4'), 69.9 (C-5''), 67.2 (C-1), 62.8 (C-6'), 41.1 (C-4), 27.3 (C-5), 25.7 (C-8), 18.8 (C-6''), 17.4 (C-9), 16.3 (C-10)

Compound 2: Ligurobustoside N (LGN)

ESI-MS  $m/z$ : 753  $[M-H]^-$ , Molecular formula:  $C_{35}H_{46}O_{18}$

$^1H$ -NMR ( $CD_3OD$ , 600 MHz)  $\delta$ : 7.81 (1H, d,  $J=15.7$  Hz, H-7'''), 7.32 (2H, d,  $J=8.7$  Hz, H<sub>2</sub>-2, 6), 7.28 (1H, d,  $J=2.2$  Hz, H-2'''), 7.17 (1H, dd,  $J=2.2, 8.3$  Hz, H-6'''), 7.05 (1H, d,  $J=8.3$  Hz, H-5'''), 6.92 (2H, d,  $J=8.7$  Hz, H<sub>2</sub>-3, 5), 6.52 (1H, d,  $J=15.7$  Hz, H-8'''), 5.36 (1H, d,  $J=1.6$  Hz, H-1''), 5.23 (1H, d,  $J=1.7$  Hz, H-1'''), 5.15 (1H, t,  $J=9.5$  Hz, H-4'), 4.45 (1H, d,  $J=7.3$  Hz, H-1'), 4.12 (1H, m, H<sub>b</sub>-8), 3.93 (1H, m, H<sub>a</sub>-8), 3.11 (2H, t,  $J=6.7$  Hz, H<sub>2</sub>-7), 1.31 (3H, d,  $J=6.5$  Hz, H<sub>3</sub>-6''), 1.23 (3H, d,  $J=6.4$  Hz, H<sub>3</sub>-6''')

$^{13}C$ -NMR ( $CD_3OD$ , 150 MHz)  $\delta$ : 168.7 (C=O), 156.9 (C-4), 150.7 (C-4'''), 148.3 (C-7'''), 146.9 (C-3'''), 131.6 (C-2, 6), 130.8 (C-1), 127.7 (C-1'''), 124.5 (C-6'''), 117.3 (C-5'''), 116.5 (C-3, 5), 115.7 (C-2'''), 115.1 (C-8'''), 105.1 (C-1'), 104.3 (C-1''), 102.5 (C-1'''), 81.9 (C-4''), 81.4 (C-3'), 76.9 (C-5'), 76.2 (C-2'), 75.1 (C-4'''), 74.2 (C-2'''), 72.9 (C-3'''), 72.5 (C-2''), 72.2 (C-8), 71.1 (C-3''), 70.2 (C-4'), 69.4 (C-5'', 5'''), 63.1 (C-6'), 37.3 (C-7), 19.2 (C-6''), 18.3 (C-6''')

Compound 3: Ligupurpuroside J (LPJ)

ESI-MS  $m/z$ : 759  $[M-H]^-$ , Molecular formula:  $C_{35}H_{46}O_{19}$

$^1H$ -NMR ( $CD_3OD$ , 600 MHz)  $\delta$ : 7.58 (1H, d,  $J=15.9$  Hz, H-7'''), 7.05 (1H, d,  $J=1.9$  Hz, H-2'''), 6.89 (1H, dd,  $J=8.4, 1.9$  Hz, H-6'''), 6.78 (1H, d,  $J=8.4$  Hz, H-5'''), 6.69 (1H, d,  $J=2.1$  Hz, H-2), 6.64 (1H, d,  $J=8.2$  Hz, H-5), 6.56 (1H, dd,  $J=8.0, 2.0$  Hz, H-6), 6.28 (1H, d,  $J=15.8$  Hz, H-8'''), 5.19 (1H, s, H-1''), 5.18 (1H, s, H-1'''), 4.51 (1H, dd,  $J=12.0, 1.8$  Hz, H-6'a), 4.35 (1H, d,  $J=8.1$  Hz, H-1'), 4.34 (1H,  $J=11.9, 6.3$  Hz, H-6'b), 4.13 (1H, dd,  $J=9.5, 6.2$  Hz, H-5''), 3.98 (1H, m, H-2''), 3.98 (1H, m, H-8a), 3.87 (1H, m, H-2'''), 3.87 (1H, m, H-3''), 3.74 (1H, m, H-8b), 3.73 (1H, m, H-5'''), 3.58 (1H, m, H-3'''), 3.56 (1H, m, H-5'), 3.54 (1H, m, H-4''), 3.51 (1H, m, H-3'), 3.43 (1H, m,  $J=9.9$  Hz, H-4'), 3.42 (1H, m, H-4'''), 3.33 (1H, m, H-2'), 2.78 (1H, t,  $J=7.5$  Hz, H-7), 1.28 (3H, d,  $J=6.5$  Hz, H-6'''), 1.26 (3H, d,  $J=6.5$  Hz, H-6'')

$^{13}C$ -NMR ( $CD_3OD$ , 150 MHz)  $\delta$ : 169.7 (C-9'''), 150.2 (C-4'''), 147.8 (C-7'''), 146.9 (C-3'''), 146.3 (C-4), 144.9 (C-3), 132.1 (C-1), 127.6 (C-1'''), 124.3 (C-6'''), 121.5 (C-6), 117.8 (C-2), 116.8 (C-5), 116.4 (C-5'''), 115.7 (C-2'''), 115.1 (C-8'''), 105.1 (C-1'), 103.5 (C-1''), 102.8 (C-1'''), 83.4 (C-3'), 81.9 (C-4''), 75.9 (C-2'), 75.3 (C-5'), 74.1 (C-4'''), 73.5 (C-2'''), 73.1 (C-3''), 72.9 (C-8), 72.6 (C-2''), 72.3 (C-3'''), 71.1 (C-4'), 70.2 (C-5'''), 68.5 (C-5''), 65.1 (C-6'), 37.2 (C-7), 19.3 (C-6''), 17.5 (C-6''')