Figure S1: The separation flow chart of obtained steroid saponins from *Dioscorea zingiberensis* C. H. Wright by different chromatography. When the compound is purified with HPLC, M:W represents the solvent system of acetonitrile and water, while no abbreviation of M:W represents the solvent system of methanol and water. The red numbers indicate the new steroid saponins.

Figure S2: The structural identification data of **Dioscin A** (Compound **1**). (a): HR-ESI-MS, positive ion mode; (b): UV; 190 nm-400 nm; (c): IR, 4000-0 cm^{-1}; (d): ^{1}H-NMR; (e): ^{13}C-NMR; (f): DEPT; (g): HSQC; (h): HMBC; (i): ^{1}H-^{1}H COSY; (j): NOESY; (k): HSQC-TOCSY; (l): The GC chromatography of D-Glu and L-Rha. The sugar separation was performed on a SE-30 capillary column (30 m × 0.32 mm, 0.25 μm), the temperatures of column, injection, and FID detector were set as 220 °C, 230 °C, and 240 °C, respectively. The retention time of D-Glu was 20.36 min.

Figure S3: The structural identification data of **Dioscin B** (Compound **2**). (a): HR-ESI-MS, positive ion mode; (b): UV; 190 nm-400 nm; (c): IR, 4000-0 cm^{-1}; (d): ^{1}H-NMR; (e): ^{13}C-NMR; (f): DEPT; (g): HSQC; (h): HMBC; (i): ^{1}H-^{1}H COSY; (j): NOESY; (k): HSQC-TOCSY; (l): The GC chromatography of D-Glu and L-Rha. The sugar separation was performed on a SE-30 capillary column (30 m × 0.32 mm, 0.25 μm), the temperatures of column, injection, and FID detector were set as 220 °C, 230 °C, and 240 °C, respectively. The retention time of D-Glu was 20.36 min.

Figure S4: The structural identification data of **Dioscin C** (Compound **3**). (a): HR-ESI-MS, positive ion mode; (b): UV; 190 nm-400 nm; (c): IR, 4000-0 cm^{-1}; (d): ^{1}H-NMR; (e): ^{13}C-NMR; (f): DEPT; (g): HSQC; (h): HMBC; (i): ^{1}H-^{1}H COSY; (j): NOESY; (k): HSQC-TOCSY; (l): The GC chromatography of D-Glu and L-Rha. The sugar separation was performed on a SE-30 capillary column (30 m × 0.32 mm, 0.25 μm), the temperatures of column, injection, and FID detector were set as 220 °C, 230 °C, and 240 °C, respectively. The retention time of L-Rha and D-Glu was separately 13.92 min and 20.36 min.

Figure S5: The structural identification data of **Dioscin D** (Compound **4**). (a): HR-ESI-MS, positive ion mode; (b): UV; 190 nm-400 nm; (c): IR, 4000-0 cm^{-1}; (d): ^{1}H-NMR; (e): ^{13}C-NMR; (f): DEPT; (g): HSQC; (h): HMBC; (i): ^{1}H-^{1}H COSY; (j): NOESY; (k): HSQC-TOCSY; (l): The GC chromatography of D-Glu and L-Rha. The sugar separation was performed on a SE-30 capillary column (30 m × 0.32 mm, 0.25 μm), the temperatures of column, injection, and FID detector were set as 220 °C, 230 °C, and 240 °C, respectively. The retention time of D-Glu was 20.36 min.

Figure S6: The structural identification data of **Dioscin E** (Compound **5**). (a): HR-ESI-MS, positive ion mode; (b): UV; 190 nm-400 nm; (c): IR, 4000-0 cm^{-1}; (d): ^{1}H-NMR; (e): ^{13}C-NMR; (f): DEPT; (g): HSQC; (h): HMBC; (i): ^{1}H-^{1}H COSY; (j): NOESY; (k): HSQC-TOCSY; (l): The GC chromatography of D-Glu and L-Rha. The sugar separation was performed on a SE-30 capillary column (30 m × 0.32 mm, 0.25

μm), the temperatures of column, injection, and FID detector were set as 220 °C, 230 °C, and 240 °C, respectively. The retention time of D-Glu was 20.36 min.

Figure S7: The structural identification data of **Dioscin F** (Compound **6**). (a): HR-ESI-MS, positive ion mode; (b): UV; 190 nm-400 nm; (c): IR, 4000-0 cm^{-1}; (d): ^{1}H-NMR; (e): ^{13}C-NMR; (f): DEPT; (g): HSQC; (h): HMBC; (i): ^{1}H-^{1}H COSY; (j): NOESY; (k): HSQC-TOCSY; (l): The GC chromatography of D-Glu and L-Rha. The sugar separation was performed on a SE-30 capillary column (30 m × 0.32 mm, 0.25 μm), the temperatures of column, injection, and FID detector were set as 220 °C, 230 °C, and 240 °C, respectively. The retention time of D-Glu was 20.36 min.

Figure S8: The structural identification data of **Dioscin G** (Compound **7**). (a): HR-ESI-MS, positive ion mode; (b): UV; 190 nm-400 nm; (c): IR, 4000-0 cm^{-1}; (d): ^{1}H-NMR; (e): ^{13}C-NMR; (f): DEPT; (g): HSQC; (h): HMBC; (i): ^{1}H-^{1}H COSY; (j): NOESY; (k): HSQC-TOCSY; (l): The GC chromatography of D-Glu and L-Rha. The sugar separation was performed on a SE-30 capillary column (30 m × 0.32 mm, 0.25 μm), the temperatures of column, injection, and FID detector were set as 220 °C, 230 °C, and 240 °C, respectively. The retention time of L-Rha and D-Glu was separately 13.87 min and 20.25 min.

Figure S9: The structural identification data of **Dioscin H** (Compound **8**). (a): HR-ESI-MS, positive ion mode; (b): UV; 190 nm-400 nm; (c): IR, 4000-0 cm^{-1}; (d): ^{1}H-

NMR; (e): ^{13}C-NMR; (f): DEPT; (g): HSQC; (h): HMBC; (i): ^{1}H-^{1}H COSY; (j): NOESY; (k): HSQC-TOCSY; (l): The GC chromatography of D-Glu and L-Rha. The sugar separation was performed on a SE-30 capillary column (30 m × 0.32 mm, 0.25 μm), the temperatures of column, injection, and FID detector were set as 220 °C, 230 °C, and 240 °C, respectively. The retention time of D-Glu was 20.36 min.

Figure S10: The structural identification data of **Dioscin I** (Compound **9**). (a): HR-ESI-MS, positive ion mode; (b): UV; 190 nm-400 nm; (c): IR, 4000-0 cm^{-1}; (d): ^{1}H-NMR; (e): ^{13}C-NMR; (f): DEPT; (g): HSQC; (h): HMBC; (i): ^{1}H-^{1}H COSY; (j): NOESY; (k): HSQC-TOCSY; (l): The GC chromatography of D-Glu and L-Rha. The sugar separation was performed on a SE-30 capillary column (30 m × 0.32 mm, 0.25 μm), the temperatures of column, injection, and FID detector were set as 220 °C, 230 °C, and 240 °C, respectively. The retention time of D-Glu was 20.36 min.

Figure S11: The representative membrane protein blots of anti-inflammatory and anti-I/R effects on rats (a), RAW 264.7 (b), and PC12 (c) *in vivo* and *in vitro*, respectively, of n-butanol extracts and obtained Compound **1**, **2**, and **7**. (i) NF-κB of n-butanol extracts; (ii) β-actin of n-butanol extracts; (I) NF-κB of Compound **1**; (II) β-actin of Compound **1**; (III) NF-κB of Compound **2**; (IV) β-actin of Compound **2**; (V) NF-κB of Compound **7**; (VI) β-actin of Compound **7**