Supporting Information

Prenylated Phenolic Compounds from the Aerial Parts of Glycyrrhiza uralensis as PTP1B and α-Glucosidase Inhibitors

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1. The detailed isolation procedure of compounds 11-86.

The dried plant materials (10 kg) were powdered and successively extracted with 90\% EtOH (20L × 2h × 2) and 70\% EtOH (20L × 2h × 2) under reflux to yield the EtOH extract. After concentration under vacuum, the extract was dispersed in H₂O and extracted successively with petroleum ether, EtOAc, and n-BuOH. The EtOAc extract (300 g) was subjected to a silica gel column and eluted with petroleum ether-EtOAc (1:0-0:1, v/v) to obtain fractions A-H.

Fraction D (16.8 g) was separated on a silica gel column eluted with petroleum ether-EtOAc (50:1 to 0:1, v/v) to obtain fractions DA-DF. Fraction DC (8.8 g) was subjected to silica gel column chromatography eluted with petroleum ether-EtOAc (100:1 to 0:1, v/v) to provide fractions DCA-DCF. Fraction DCB (4.2 g) was subjected to polyamide and Sephadex LH-20 column chromatography successively, then further purified by semipreparative HPLC on a YMC Pack ODS-A column to give compound 19 (5.19 mg), 20 (30.67 mg), 21 (24.40 mg), 22 (2.05 mg), 23 (2.31 mg), 24 (4.50 mg), 25 (4.71 mg) and 26 (3.48 mg). Fraction DCC (55.0 mg) was subjected to silica gel and Sephadex LH-20 column chromatography successively, then further was purified by semipreparative HPLC on the same YMC column to afford compound 26 (2.09 mg), 27 (1.07 mg) and 28 (2.44 mg). Fraction DD (3.2 g) was subjected to polyamide column chromatography eluted with CH₂Cl₂-MeOH (100:1 to 0:1, v/v) to provide fractions DDA-DDC. Fraction DDA (800.4 mg) was subjected to Sephadex LH-20 column chromatography and purified by semipreparative HPLC on a YMC Pack ODS-A column to give compound 31 (32.47 mg), 32 (13.62 mg) and 33 (1.04 mg). Fraction DDB (1.2 g) was subjected to Sephadex LH-20 column chromatography and purified by semipreparative HPLC on a YMC Pack ODS-A column to give compound 18 (1.02 mg), 29 (1.95 mg), 30 (2.60 mg) and 34 (1.04 mg). Fraction DE (2.1 g) was subjected to Sephadex LH-20 column chromatography eluted with MeOH to provide fractions DEA-DED. Fraction DEC (40.3 mg) was further purified using semipreparative HPLC on the same YMC column to afford 18 (0.65 mg).
Fraction E (30.1 g) was subjected to silica gel column chromatography to produce fractions EA-ED, eluted with a gradient of petroleum ether-EtOAc (1:0 to 0:1, v/v). Fraction EB (4.3 g) was subjected to polyamide column chromatography and eluted with CH$_2$Cl$_2$-MeOH (1:0 to 5:1, v/v) to obtain fractions EBA-EBE. Fraction EBC (2.2 g) was subjected to Sephadex LH-20 column chromatography with MeOH as eluent followed by semipreparative HPLC to afford 14 (1.23 mg), 15 (3.68 mg), 16 (1.02 mg) and 17 (1.23 mg). Fraction EBE (793.6 mg) was purified by semipreparative HPLC to afford 13 (1.02 mg). Fraction EC (1.3 g) was subjected to polyamide column chromatography eluted with CH$_2$Cl$_2$-MeOH (1:0 to 5:1, v/v) to provide fractions ECA-ECE. Fraction ECD (98.2 mg) was subjected to Sephadex LH-20 column chromatography and then further purified using semipreparative HPLC on the same YMC column to afford 11 (55.58 mg) and 12 (3.84 mg).

Fraction F (28.4 g) was applied to a silica gel column and eluted with petroleum ether-EtOAc (1:0 to 1:1, v/v) to yield fractions FA-FE. Fraction FB (10.8 g) was applied to a silica gel column and eluted with petroleum ether-EtOAc (100:1 to 1:1, v/v) to yield fractions FBA-FBD. Fraction FBA (5.4 g) was subjected to polyamide column chromatography using a CH$_2$Cl$_2$-MeOH (1:0 to 25:1, v/v) gradient elution, then purified over Sephadex LH-20 eluted with MeOH, followed by semipreparative HPLC on a YMC Pack ODS-A column to give 67 (13.82 mg), 68 (1.47 mg), 69 (9.14 mg), 70 (18.87 mg), 71 (1.25 mg), 72 (47.75 mg), 73 (1.25 mg) and 74 (1.80 mg) respectively. Fraction FBB (3.7 g) was subjected to polyamide column chromatography then purified over Sephadex LH-20 eluted with MeOH, followed by semipreparative HPLC on a YMC Pack ODS-A column to give 51 (3.15 mg). Fraction FC (2.2 g) was subjected to polyamide column chromatography using a CH$_2$Cl$_2$-MeOH (1:0 to 50:1, v/v) to give fraction FCA-FCE. Fraction FCD (800.3 mg) was subjected to polyamide column chromatography with CH$_2$Cl$_2$-MeOH (1:0 to 25:1, v/v) as eluent to give fractions FCDA-FCDD. Fraction FCDC (297.6 mg) was further purified by semipreparative HPLC (MeCN-H$_2$O, 48:52, v/v) to give 38 (3.51 mg), 43 (0.82 mg), 44 (1.25 mg) and 45 (2.44 mg). Fraction FCDD (100.4 mg) was further purified by semipreparative HPLC (MeCN-H$_2$O, 48:52, v/v) to afford 39 (4.04 mg).
40 (1.66 mg), 41 (10.26 mg) and 42 (2.76 mg). Fraction FD (12.1 g) was applied to a silica gel column and eluted with petroleum ether-EtOAc (10:0 to 1:1, v/v) to yield fractions FDA-FDG. Fraction FDC (3.3 g) was subjected to Sephadex LH-20 eluted with MeOH, followed by semipreparative HPLC on a YMC Pack ODS-A column to give 55 (14.82 mg), 56 (15.59 mg), 60 (18.16 mg), 64 (1.02 mg) and 66 (1.01 mg). Fraction FDD (2.6 g) was applied to a silica gel column and eluted with petroleum ether-EtOAc (10:0 to 1:1, v/v) to yield fractions FDDA-FDDE. Fraction FDDA (116.8 mg) was further purified by semipreparative HPLC (MeCN-H2O, 40:60, v/v) to give 52 (3.58 mg). Fraction FDDB (314.6 mg) was further purified by semipreparative HPLC (MeCN-H2O, 55:45, v/v) to afford 64 (1.52 mg) and 65 (18.24 mg). Fraction FDDC (559.8 mg) was further purified by semipreparative HPLC to give 57 (19.67 mg), 58 (44.40 mg), 59 (1.66 mg), 62 (3.35 mg) and 63 (1.72 mg). Fraction FDDD (189.2 mg) was further purified by semipreparative HPLC to afford 53 (14.82 mg), 54 (2.28 mg), 55 (14.82 mg) and 56 (15.59 mg). Fraction FDDE (236.2 mg) was further purified by semipreparative HPLC (MeCN-H2O, 55:45, v/v) to afford 60 (18.16 mg) and 61 (1.25 mg).

Fraction G (28.1 g) was fractionated by silica gel column chromatography eluted with a gradient of petroleum ether-EtOAc (1:0 to 1:1, v/v) to give three fractions GA-GF. Fraction GB (12.4 g) was subjected to polyamide column chromatography then followed by semipreparative HPLC on a YMC Pack ODS-A column to give 79 (3.40 mg). Fraction GC (5.4 g), eluted with CH2Cl2-MeOH (1:0 to 25:1, v/v), was separated on a polyamide column to yield fractions GCA-GCE. Fraction GCD (76.4 mg) was purified over Sephadex LH-20 using MeOH as solvent, followed by semipreparative HPLC on a YMC Pack ODS-A column (5 µm, 250×10 mm; flow rate, 2 mL/min; MeCN-H2O, 55:45, v/v) to obtain 86 (1.63 mg). Fraction GD (6.2 g) was subjected to polyamide column chromatography then purified over Sephadex LH-20 eluted with MeOH, followed by semipreparative HPLC on a YMC Pack ODS-A column to give 78 (5.46 mg), 81 (3.09 mg), 82 (3.74 mg), 83 (12.87 mg), 84 (21.19 mg) and 85 (1.38 mg). Fraction GF (8.3 g) was subjected to polyamide column chromatography to yield fractions GFA-GFF. Fraction GFB (2.1 g) was subjected to
polyamide column chromatography then purified over Sephadex LH-20 eluted with MeOH, followed by semipreparative HPLC on a YMC Pack ODS-A column to give 75 (26.12 mg), 76 (23.60 mg), 77 (33.42 mg) and 80 (3.58 mg).
2. The ECD spectra computational section of compound 1.

The calculation of ECD spectra of all the compounds consists in conformational search by molecular mechanics (MM), a subsequent DFT geometry optimization and the determination of chiroptical theoretical properties by TD-DFT.[1]

The MMFF94s force field and the Sybyl-X2.0 software were used for MM calculations.[2,3] The conformational search performs random search algorithm to identify the preliminary conformers. All MM conformers within an energy cutoff of 10 kcal/mol were identified as the input structures for geometry optimizations.

DFT calculations were performed using the Gaussian 16 software.[4] Geometry optimization and frequency calculations were carried out at the CAM-B3LYP/6-311+G(d,p) level, and the PCM solvation model for MeOH was used to account for long-range solvation effects.[5,6]

TD-DFT calculations were also carried out using the Gaussian 16 software. The CAM-B3LYP was employed in combination with 6-311+G(d,p) basis set and the PCM solvation model for MeOH.[7] Calculations were performed on all optimized conformers having a Boltzmann equilibrium population at 298.15 K and 1 atm above 1%.

The theoretical UV and ECD spectra of optimized conformers were derived by approximation of oscillator strength ($f_j$) and rotational strength in dipole velocity formalism ($R_j$) which calculated for the lowest-energy electronic transitions to a Gaussian bands with a $\Delta\sigma$ value of 0.25 eV. The theoretical UV and ECD spectra of compounds were derived as the weighted average of the contribution of all conformers according to their Boltzmann equilibrium populations at 298.15 K and 1 atm derived from free energies, and compared to the corresponding experimental spectra.

Reference:


3. [Rh$_2$(OCOCF$_3$)$_4$]-induced ECD experiments of compound 6 and 7.

Compound 6 and 7 (0.50mg) were dissolved in the anhydrous DMSO (0.277 mL), respectively. Rh$_2$(OCOCF$_3$)$_4$ was dissolved in the anhydrous DMSO at 1.2mg/mL. The ECD spectra of compound in DMSO were recorded firstly. Then the ECD spectra of compound with Rh$_2$(OCOCF$_3$)$_4$ were recorded in 10min and 30 min, respectively. Comparing the experimental ECD data, the (2'S) absolute configuration in compound 6 and 7 was established by the positive Cotton effect at 320 nm based on the bulkiness rule.

Reference:


Fig. S1. (A) Changes in body weight during the experiment. Comparing to the control group, significant differences are indicated by *$p < 0.05$ and by **$p < 0.01$. (B) Organ index of white adipose tissue, liver and kidney. A, recorded after 5 weeks of treatments; B, monitored each week.
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