Supporting Information to:

Spiraeosides A and B, Two New Diterpenoid Glucosides from

*Spirea japonica var. ovalifolia*

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General experimental procedures

Melting points were determined using a Kofler micro-melting point apparatus and are uncorrected. Optical rotations were determined on a Horiba SEPA-300 polarimeter. IR spectra
were obtained on KBr pellets using a Bio-Rad FTS-135 spectrophotometer. 1D and 2D NMR spectra were recorded on Bruker AM-400 and Bruker DRX-500 spectrometers, respectively, using TMS as internal standard. EI-MS, FAB-MS, and HR-FAB-MS measurements were carried out on a VG Auto Spec-3000 spectrometer. Column chromatography was performed on silica gel H (10–40 μm; Qingdao Marine Chemical Factory), Sephadex LH-20 (40–70 μm, Amersham Pharmacia Biotech AB, Uppsala, Sweden), and macroporous resin (D-101 type, 500 μm; Tianjin, China).

Compound 1: Colorless needles (MeOH), m.p. 267–268 °C, [α]D23: −70.31 (c 2.55, MeOH); IR (KBr): 3494 (OH), 2958, 1380, 1377, 1171, 1075, 1031, 1032, 960, 900 cm⁻¹; EI-MS: m/z = 332 (M − C₆H₁₀O₅, 13), 315 (M − OH − C₆H₁₀O₅, 32), 286 (M − 315 − CH₃, 100), 268 (15), 257 (23), 239 (30), 201 (12), 180 (3), 163 (C₆H₁₀O₅, 5), 159 (20), 131 (20), 105 (25), 91 (41), 73 (64); FAB-MS: m/z = 493 (M − H, 42), 331 (M − C₆H₁₁O₅, 70), 315 (M − OH − C₆H₁₀O₅, 7), 161 (100); HR-FAB-MS: m/z = 493.2407 (calcd. for C₂₆H₃₇O₉: 493.2438).

Compound 2: Crystalline solid (MeOH), m.p. 280–281 °C, [α]D23: −4.13 (c 2.42, MeOH); IR (KBr): 3334 (OH), 2927, 1726 (C=O), 1380, 1317, 1132, 1074, 1039, 1021, 912, 824 cm⁻¹; EI-MS: m/z = 332 (M − C₆H₁₀O₅, 13), 315 (M − OH − C₆H₁₀O₅, 45), 298 (M − 2OH − C₆H₁₀O₅, 43), 286 (M − 315 − CH₃, 20), 270 (38), 256 (15), 239 (22), 202 (23), 180 (5), 163 (C₆H₁₀O₅, 7), 159 (19), 131 (38), 105 (47), 91 (89), 73 (100); FAB-MS: m/z = 493 (M − H, 100), 331 (M − C₆H₁₁O₅, 40), 315 (M − OH − C₆H₁₀O₅, 16), 161 (17); HR-FAB-MS: m/z = 493.2407 (the same as that of 1).

**Enzymatic hydrolysis of 1 and 2**

A solution of 1 (5 mg) and β-D-glucosidase (10 mg) in acetate buffer (5 mL, pH 5) was incubated at 37 °C for 5 days followed by extraction with Et₂O. The Et₂O layer contained 1a and 2a by TLC (on a silica gel H plate, petroleum–EtOAc, 5:1), and the aqueous layer contained glucose by TLC (on a microcrystalline cellulose plate, n-BuOH–pyridine–H₂O, 6:4:3), which were in agreement with the corresponding authentic samples.
X-ray crystal structure analysis of 1 [1]

Crystal data: C_{26}H_{38}O_{9}, MW 494.56; monoclinic, space group P2_12_12_1; a = 11.4146 (4), b = 7.3288 (2), c = 13.9662 (6) Å. Crystal shape/crystal color: plate/colorless; V = 1159.70 (7) Å³; Z = 2; D_{calc} = 1.165 g/cm³; Mo Kα (λ = 0.71073 Å). The data were collected on a NONIUS Kappa CCD diffractometer with a graphite monochromator. Mo Kα radiation using a colorless crystal with dimensions of 0.40 × 0.27 × 0.10 mm³: maximum 2θ value 54.97°; reflections collected/unique: 22024/5255 [R (int.) = 0.0669]; reflections with I > 2σ(I): 3688.

Refinement method: full-matrix least-squares on F² (goodness-of-fit on F²: 0.972); data/restraints/parameters: 5255/1/322. The structure was solved by the direct method SHELX-97 and expanded using difference Fourier techniques and was refined by the program SHELXL-97 and full-matrix least-squares calculations. Hydrogen addition/treatment: geom./mixed. The final R indices [I > 2σ(I)] were R1 (F) = 0.0443 and wR2 (F²) = 0.0772.

The CCDC deposit number is 184690.

References

1 Crystallographic data for compound 1 have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). Copies can be obtained on request, free of charge, by quoting the publication citation and the deposit number 184690.
Fig. 1S $^1$H-NMR spectrum of spiraeoside A (1) in C$_3$D$_3$N.
Fig. 2S $^{13}$C-NMR spectrum of spiraeoside A (1) in C$_5$D$_5$N.
Fig. 3S HSQC spectrum of spiraeoside A (1) in C$_3$D$_5$N.
Fig. 4S HMBC spectrum of spiraeoside A (1) in C$_3$D$_3$N.
Fig. 5S COSY spectrum of spiraeoside A (1) in C$_3$D$_5$N.
Fig. 6S ROESY spectrum of spiraeoside A (1) in C₅D₅N.
Fig. 7S FAB-MS spectrum of spiraeoside A (1).
Fig. 8S IR spectrum of spiraeoside A (1).
Fig. 9S $^1$H-NMR spectrum of spiraeoside B (2) in C$_3$D$_3$N.
Fig. 10S $^{13}$C-NMR spectrum of spiraeoside B (2) in C$_5$D$_3$N.
Fig. 11S HSQC spectrum of spiraeoside B (2) in C₅D₅N.
Fig. 12S HMBC spectrum of spiraeoside B (2) in C$_5$D$_5$N.
Fig. 13S COSY spectrum of spiraeoside B (2) in C$_5$D$_5$N.
Fig. 14S FAB-MS of spiraeoside B (2).
Fig. 15S IR spectrum of spiraeoside B (2).