Supporting Information

Gentiobiosylation of β-Resorcylic Acid Esters and Lactones: First Synthesis and Characterization of Zearalenone-14-β,β-D-Gentiobioside

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1) Experimental details – General remarks

All reactions were performed under an argon atmosphere. The progress of reactions was monitored by thin-layer chromatography (TLC) over silica gel 60 F254 (Merck). The chromatograms were visualized by irradiation with ultraviolet light or by heat staining with ceric ammonium molybdate in ethanol/sulfuric acid. LC-ESI-MS data in full scan mode were obtained on an HCT ion trap mass spectrometer (Bruker, Germany). For chromatographic separation a 1200 series HPLC system (Agilent Technologies, Germany) equipped with a Luna RP-C18 column (3.0 x 150 mm, 3 μm particle size, Phenomenex, Germany) was used. A linear acetonitrile/water gradient (10-90% acetonitrile) containing 0.1% acetic acid and a flow rate of 1 mL/min were applied. Application of pure substances was achieved using a TLC-MS interface (Camag, Germany). Preparative HPLC separation was done on an 1100 Series preparative HPLC system (Agilent Technologies, Germany) using a SunFire Prep C18 OBD, 5 μm, 19x100 mm column (Waters, Germany). Eluents were composed of water, MeOH and glacial acetic acid (A: 79.5:20:0.5, v:v:v; B: 0:99.5:0.5, v:v:v) and the flow rate was 16 mL/min. After an initial hold time at 30% B for 0.1 min, the proportion of B was linearly increased to 70% within the next 12.9 min, and to 100%B within another 0.1 min. Thereafter, the column was flushed with 100% B for 1.8 min followed by column re-equilibration at 30%B for 2 min. To obtain LC-HR-MS/MS spectra an 6550 iFunnel Q-TOF instrument after electrospray ionization was used in combination with a 1290 Infinity UHPLC system (both Agilent Technologies, Germany). The UHPLC-system was equipped with a Zorbax SB C18 Rapid Resolution High Definition column (150 mm x 2.1 mm, 1.8 μm particle size, Agilent Technologies, Germany) and was operated with a MeOH-water gradient containing 0.1 % formic acid. Preparative column chromatography was performed on silica gel 60 (40-63 μm, Merck, Germany) using a Sepacore™ Flash System (Büchi, Switzerland). "H and 13C NMR spectra were recorded on an Avance DRX-400 MHz spectrometer (Bruker, Germany). Data were recorded and evaluated using TOPSPIN 1.3 (Bruker Biospin). All chemical shifts are given in ppm relative to tetramethylsilane. The calibration was done using residual solvent signals. Zearalenone was obtained from Fermentek (Israel) and all other chemicals were purchased from ABCR (Germany), Sigma-Aldrich (Austria/Germany) or Carbosynth (UK).
2) NMR spectra of ZEN-14-β,α-gentiobioside (3)

a) $^1$H NMR ($d_6$-DMSO, 400 MHz)

b) $^{13}$C NMR ($d_6$-DMSO, 100 MHz)
c) HH-COSY ($d_6$-DMSO, 400 MHz)
3) HR-MS spectra of ZEN-14-β, D-gentiobioside (3)

HR-MS/MS analysis showed preferred fragmentation of the glycosidic bond between zearalenone and the glycon. Stepwise cleavage of both glucosyl moieties was not observed, which can be used as a distinctive feature between ZEN-14-β, D-gentiobioside and ZEN-14,16-di(β, D-glucoside) during MS analysis.