Supplementary Information

**Phytoalexins from the crucifer rutabaga: structures, syntheses, biosyntheses and antifungal activity**

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Supplementary Information

Table of Contents:

Experimental general

Synthesis of compounds 17, 18, 19, 24a

Spectral data for compound 9

Experimental general S1

Synthesis of compounds 17, 18, 19, 24a S1-S4

Spectral data for compound 9 S4
Experimental

General. All solvents were HPLC grade and used as such, except for CH₂Cl₂ and CHCl₃ which were redistilled and THF which was dried over Na and benzophenone. Flash CC: C-18 reversed phase silica gel 40 µm. Analytical HPLC analysis was carried out with a high performance liquid chromatograph equipped with quaternary pump, automatic injector, and photodiode array detector (wavelength range 190-600 nm), degasser, and an ODS column (5 µm particle size silica, 4.6 i.d. x200 mm), equipped with an in-line filter. Mobile phase: H₂O-CH₃CN, 75:25 to 100% CH₃CN, for 35 min, linear gradient, and flow rate 1.0 mL/min. Other conditions as previously reported.

**1-Boc-2-chloroindole-3-carboxylic acid (17).** 1-Boc-2-chloroindole-3-carboxaldehyde (16, 0.56 g, 2 mmol) was dissolved in the mixture of t-butanol (10 mL) and 2-methylbut-2-ene (10 mL). A solution of NaClO₂ (1.81 g, 20 mmol) and KH₂PO₄ (2.04 g, 15 mmol) in water (10 mL) was then added and the mixture was vigorously stirred at rt. After 2 h the organic layer was separated, the aq layer was extracted with CH₂Cl₂-MeOH (95:5), the combined organic extracts were dried (Na₂SO₄) and the solvent evaporated under reduced pressure. Crystallization (CH₂Cl₂-hexane) afforded 0.567 g (96%) of colorless powder. Mp 175 – 177 °C; HPLC tₘ = 19.8 min; ¹H NMR (500 MHz, CDCl₃): 12.68 (br s, 1H, D₂O exchangeable), 8.25 (m, 1H), 8.04 (m, 1H), 7.38 (m, 2H), 1.74 (s, 9H); ¹³C NMR (125 MHz, CDCl₃): 168.9 (s), 148.3 (s), 135.2 (s), 132.7 (s), 126.2 (s), 125.5 (d), 124.6 (d), 121.8 (d), 114.6 (d), 109.5 (s), 86.8 (s), 28.3 (q); HREIMS m/z (% relative abundance) measured: 295.0607 (295.0611 calcd for C₁₄H₁₄ClNO₄); EIMS m/z (% relative abundance): 295 [M⁺]⁺ (6), 221 (5), 195 (37), 130 (7). FTIR νₘₚ: 2979, 1745, 1683, 1532, 1445, 1308, 1206, 1150, 745 cm⁻¹.

**Methyl 1-Boc-2-chloroindole-3-carboxylate (18).** 1-Boc-2-chloroindole-3-carboxylic acid (17, 74 mg, 0.25 mmol) was dissolved in ethereal diazomethane solution (3 mL) and
Supplementary Information

stirred for 5 minutes at rt. The excess of diazomethane was quenched with acetic acid and the solvent was evaporated under reduced pressure. The colorless oil (77 mg, 100%) was obtained, sufficiently pure to use in the next step. HPLC $t_R = 35.1$ min; $^1$H NMR (500 MHz, CDCl$_3$): 8.12 (d, $J = 8$ Hz, 1H), 8.04 (d, $J = 8$ Hz, 1H), 7.35 (m, 2H), 4.00 (s, 3H), 1.73 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): 164.0 (s), 148.5 (s), 135.2 (s), 131.1 (s), 126.1 (s), 125.3 (d), 124.3 (d), 121.5 (d), 114.7 (d), 110.5 (s), 86.5 (s), 51.8 (q), 28.3 (q); HREIMS $m/z$ (% relative abundance) measured: 309.0765 (309.0768 calcd for C$_{15}$H$_{16}$ClNO$_3$); EIMS $m/z$ (% relative abundance): 309 [M$^+$] (20), 252 (6), 236 (13), 209 (100), 178 (23), 148 (5), 114 (22). FTIR $\nu_{\text{max}}$: 2980, 1749, 1722, 1532, 1446, 1309, 1147, 747 cm$^{-1}$.

**Methyl 1-Boc-2-chloroindole-3-carboxamide (19).** Thionyl chloride (30 μL, 0.45 mmol) was added to a solution of acid 17 (90 mg, 0.3 mmol) in dry THF (3 mL) under Ar atmosphere and the mixture was stirred at rt. After 3 h the reaction mixture was cooled to 0 °C, a solution of MeNH$_2$ in THF (2 M, 4 mL, 8 mmol) was added and the mixture was stirred for further 20 min at 0 °C. Then, the reaction mixture was diluted with brine (30 mL), extracted with EtOAc, the combined organic extract was dried (Na$_2$SO$_4$), the solvent evaporated under reduced pressure and the residue chromatographed on silica gel (hexane-acetone, 2:1). Evaporation of the solvent afforded a colorless oil (79 mg, 85%). An analytical sample was obtained by crystallization from CH$_2$Cl$_2$-hexane. Mp 92 – 94 °C; HPLC $t_R = 20.9$ min; $^1$H NMR (500 MHz, CDCl$_3$): 8.18 (d, $J = 8$ Hz, 1H), 8.02 (d, $J = 8$ Hz, 1H), 7.34 (m, 2H), 6.50 (br s, 1H, D$_2$O exchangeable), 3.08 (d, $J = 5$ Hz, 3H), 1.72 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): 163.6 (s), 148.7 (s), 135.2 (s), 126.8 (s), 125.5 (d), 124.2 (d), 123.8 (s), 121.5 (d), 114.8 (s), 114.7 (d), 86.2 (s), 28.3 (q), 26.6 (q); HREIMS $m/z$ (% relative abundance) measured: 308.0923 (309.0928 calcd for C$_{15}$H$_{17}$ClN$_2$O$_3$); EIMS $m/z$ (% relative abundance): 308 [M$^+$] (6), 208 (37), 178 (29), 149 (15). FTIR $\nu_{\text{max}}$: 3291, 2977, 1743, 1643, 1546, 1447, 1309, 1154, 747 cm$^{-1}$. 

S3 of S4
[2,4,5,6,7-D₅]-Tryptamine (24a). [2,4,5,6,7-D₅]-Tryptamine was synthesized from [2,4,5,6,7-D₅]-L-tryptophan (50.9 mg, 0.24 mmol) as previously reported for the non-labeled compound to afford [2,4,5,6,7-D₅]-tryptamine (25.2 mg, 0.15 mmol, 62%). ¹H NMR (500 MHz, CD₃OD): δ 2.90 (m, 4H). HRMS-EI m/z (% relative abundance): measured 165.1315 (20), calculated for [M]⁺ (C₁₀H₇D₅N₂) 135.0967 (100). FTIR ν_max: 3302, 1670 cm⁻¹.

Isalexin (9). HPLC t_R = 3.7 min; ¹H NMR (500 MHz, CD₃CN): 8.82 (br s, 1H, D₂O exchangeable), 7.52 (dd, J = 8, 8 Hz, 1H), 6.67 (d, J = 8 Hz, 1H), 6.50 (d, J = 8 Hz, 1H), 3.91 (s, 3H); ¹³C NMR (125 MHz, CD₃CN): 181.7 (s), 160.8 (s), 160.0 (s), 152.3 (s), 142.0 (d), 108.4 (d), 107.8 (s), 105.6 (d), 57.2 (q); HREIMS m/z (% relative abundance) measured: 177.0422 (177.0426 calcld for C₉H₇NO₃); EIMS m/z (% relative abundance): 177 [M]⁺ (83), 149 (100), 122 (35), 107 (42), 63 (9). FTIR ν_max: 3321, 1748, 1717, 1620, 1601, 1493, 1244, 1101, 775 cm⁻¹. UV λ_max (log ε) 199 (4.2), 234 (3.9), 335 (3.4).