Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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First Syntheses of Biologically Active Fungal Metabolites Pestalotiopsones A, B, C and F.

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General Experimental Conditions

Apparatus

^{1}H and ^{13}C NMR spectra were recorded at 298 K, at 300 MHz or 400 MHz and 75 MHz or 100 MHz respectively, on an Inova 300, Varian Mercury 300 or Varian MR-400 instrument. Chemical shifts are reported in ppm (δ). ^{1}H NMR spectra are referenced to the resonance from residual $CHCl_3$ at 7.26 ppm, the central peak in the resonance from residual CHD_2COCD_3 at 2.05 ppm and the central peak in the signal from residual CHD_2OD at 3.31 ppm. ^{13}C NMR spectra are referenced to the central peak in the signal from $CDCl_3$ at 77.0 ppm, the central peal in the resonance from $(CD_3)_2CO$ at 29.8 ppm and the central peak in the signal from CD_3OD at 49.0 ppm. The appearance and multiplicities of ^{1}H resonances are expressed by the abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and combinations thereof for more highly coupled systems. ^{13}C NMR were run as proton decoupled spectra. ^{1}H signals and ^{13}C signals where appropriate are described by chemical shift δ (integration, multiplicity, $|J|$ (Hz), assignment). EI-MS and HREI-MS were recorded on a VG autospec mass spectrometer or Waters autospec premier mass spectrometer, operating at 70 eV. ESI-MS and HRESI-MS were recorded on a Bruker Apex 3. Positive ionisation was detected unless otherwise indicated. Mass/charge ratios (*m/z*) are reported and relative abundance of the ions as percentage of base peak intensity. IR spectra were recorded on a Bruker Alpha-P ATR as neat solid or film. Characteristic peaks (ν_{max}) are recorded in wavenumbers. UV spectra were measured on a Cary 4G UV-Visible Spectrophotometer using a 1 cm solution cell in the solvent indicated. Spectra maxima are recorded in nm (logε). Microwave reactions were carried out using an Explorer CEM Automated Microwave Workstation in 10 mL reaction vessels at the wattage and pressure stated.

Chromatography

Thin layer chromatography (TLC) was run on Merck silica gel 60 F_{254} aluminium backed plates, and were run in the eluting system described for each plate. Plates were viewed under UV light (254 nm) and/or by developing in potassium permanganate (100 mL water, 1 g $KMnO_4$, 6 g K_2CO_3, 0.2 g NaOH) or ceric phosphomolybdic acid (100 mL water, 5 g $12MoO_3.H_3PO_4$, 0.6 g $Ce(SO_4)_2$, 6 mL conc. H_2SO_4) dip. Flash chromatography was performed under pressure using silica gel (230–400 mesh Scharlau 60) as solid support and HPLC-graded solvents as eluent. Semi-preparative HPLC was performed using an Agilent 1100 system, utilising a Phenomex LUNA 5μ C18 250 × 10.00 mm column and an Agilent 1100 series diode array detector for eluate detection. Elution was carried out using milli-Q water and pre-filtered (0.45 μm nylon membrane filter) methanol in a 30 % v/v water/methanol solution at 1.5 mL/min with detection at 243 nm.

Solvents and reagents

In general reagents were purchased from commercial suppliers and used without further purification unless otherwise stated. All solvents were dried and distilled either immediately prior to use or stored as appropriate. Ethereal solvents Et_2O and THF were refluxed over sodium and benzophenone. Toluene was refluxed over sodium, CH_2Cl_2 was refluxed with and distilled from CaH_2 and acetone was refluxed with and distilled from Na_2SO_4.

7
^{1}H NMR
300 MHz
$CDCl_3$

7.26, 4.77, 3.67, 3.58, 2.87, 2.80, 2.77, 2.71

ppm

7
^{13}C NMR
75 MHz
$CDCl_3$

180.98, 171.47, 154.29, 94.05, 77.52, 77.10, 76.68, 54.63, 51.74, 47.88, 45.76, 31.15

ppm

7.26
6.44
6.43
6.38
6.37
6.36
3.78
3.69
3.56

8
^1H NMR
300 MHz
$CDCl_3$

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0
ppm

171.89
160.91
136.09
107.40
99.28
77.52
77.10
76.68
55.38
52.16
41.53

^{13}C NMR
75 MHz
$CDCl_3$

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40
ppm

7.26
6.40
6.40
6.34
6.34
3.82
3.80
3.68
3.66
2.49

^{1}H NMR
300 MHz
$CDCl_3$

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
ppm

203.77
171.77
161.63
159.46
134.98
123.69
108.29
97.53
77.52
77.10
76.68
55.65
55.44
51.99
39.11
32.26

9
^{13}C NMR
75 MHz
$CDCl_3$

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

^{1}H NMR
300 MHz
$CDCl_3$

13.06, 7.26, 6.38, 6.38, 6.32, 6.31, 3.90, 3.81, 3.72, 2.60

ppm: 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0

^{13}C NMR
100 MHz
$CDCl_3$

203.36, 171.36, 166.26, 164.10, 136.79, 115.42, 112.86, 100.42, 77.42, 77.10, 76.78, 55.49, 52.50, 41.76, 32.00

ppm: 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30

7.26, 6.39, 6.38, 6.34, 6.33, 4.40, 4.38, 3.94, 3.91, 3.86, 3.81, 3.70, 2.67, 2.62, 2.58, 2.57, 2.56, 2.52, 1.79, 1.65, 1.51, 1.25, 0.88

^{1}H NMR
300 MHz
$CDCl_3$

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

192.37, 171.78, 165.10, 164.50, 138.40, 113.89, 113.33, 100.40, 77.58, 77.52, 77.10, 76.68, 55.52, 51.81, 43.61, 41.14, 34.88, 31.79, 29.19, 24.89, 22.66, 14.11

11
^{13}C NMR
75 MHz
$CDCl_3$

77.58, 77.52, 77.10, 76.68

77.5 77.0 76.5
ppm

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

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7.26 6.78 6.77 6.69 6.68 6.00 4.14 3.87 3.72 2.55 2.53 2.50 1.71 1.69 1.66 1.28 0.90 0.88 0.86

13
^{1}H NMR
300 MHz
$CDCl_3$

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

179.14 171.82 167.76 162.51 159.64 137.12 117.50 115.97 110.61 99.88 77.52 77.10 76.68 55.66 51.82 40.90 33.74 31.66 28.95 26.72 22.60 14.06

13
^{13}C NMR
75 MHz
$CDCl_3$

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

7.26, 6.39, 6.38, 6.34, 6.33, 4.40, 4.39, 3.99, 3.94, 3.91, 3.86, 3.81, 3.70, 2.67, 2.62, 2.58, 2.56, 2.52, 1.81, 1.65, 1.32, 1.25, 0.90

12
^{1}H NMR
300 MHz
$CDCl_3$

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

192.47, 171.84, 165.14, 164.54, 138.43, 113.93, 113.35, 100.43, 77.61, 77.52, 77.10, 76.68, 55.57, 51.86, 43.61, 41.18, 34.87, 31.62, 24.58, 22.59, 14.05

12
^{13}C NMR
75 MHz
$CDCl_3$

77.61, 77.52, 77.10, 76.68

78.0 77.5 77.0 76.5 76.0
ppm

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

7.26, 6.77, 6.76, 6.68, 6.67, 6.00, 4.14, 3.87, 3.71, 2.55, 2.52, 2.50, 1.72, 1.69, 1.67, 1.38, 1.36, 1.25, 0.90

14
^{1}H NMR
300 MHz
$CDCl_3$

ppm: 8.0, 7.5, 7.0, 6.5, 6.0, 5.5, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, 0.0

179.27, 171.92, 167.87, 162.59, 159.73, 137.21, 121.98, 117.59, 110.69, 99.95, 77.53, 77.10, 76.67, 55.73, 51.91, 40.98, 33.79, 31.20, 26.47, 22.41, 13.96

14
^{13}C NMR
75 MHz
$CDCl_3$

ppm: 200, 190, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10

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7.26, 6.91, 6.90, 6.83, 6.83, 6.19, 4.12, 3.89, 2.64, 2.61, 2.59, 1.74, 1.72, 1.70, 1.34, 1.29, 0.88

16
^{1}H NMR
300 MHz
$CDCl_3$

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

195.79, 181.22, 172.12, 169.96, 163.54, 160.08, 136.30, 118.18, 115.50, 110.26, 100.43, 77.36, 76.84, 56.00, 42.26, 33.95, 31.69, 26.82, 22.66, 14.13

16
^{13}C NMR
100 MHz
$CDCl_3$

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

Pestalotiopsone A (1)
^{1}H NMR
300 MHz
acetone-d_6

6.82, 6.81, 6.75, 6.74, 5.93, 4.11, 3.60, 2.62, 2.59, 2.57, 2.05, 1.74, 1.72, 1.69, 1.37, 1.28, 0.88

ppm

Pestalotiopsone A (1)
^{13}C NMR
75 MHz
acetone-d_6

179.05, 171.84, 168.38, 161.73, 160.36, 138.78, 118.58, 116.15, 110.82, 102.75, 29.65, 51.57, 40.93, 34.08, 32.44, 27.44, 23.26, 14.31

ppm

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6.81 6.80 6.74 6.74 5.93 4.10 4.08 4.06 4.04 2.61 2.59 2.56 2.06 2.05 2.04 1.74 1.72 1.70 1.37 1.29 1.22 1.20 1.17 0.88

HO O O O O

Pestalotiopsone B (2)
^{1}H NMR
300 MHz
acetone-d_6

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

178.09 170.41 167.39 160.75 159.44 138.03 117.61 115.31 109.93 101.80 59.63 40.26 33.17 31.54 26.54 22.36 13.71 13.41

HO O O O O

Pestalotiopsone B (2)
^{13}C NMR
75 MHz
acetone-d_6

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

Pestalotiopsone C (3)
^{1}H NMR
400 MHz
CD_3OD

6.78, 6.77, 6.70, 6.70, 6.04, 4.87, 4.10, 3.31, 2.64, 2.62, 2.60, 1.73, 1.59, 1.38, 1.28, 0.98, 0.97, 0.95

ppm

Pestalotiopsone C (3)
^{13}C NMR
75 MHz
CD_3OD

181.38, 173.92, 170.68, 163.39, 161.32, 138.70, 119.63, 115.60, 110.40, 102.96, 49.00, 41.79, 34.58, 32.85, 27.87, 23.65, 14.38

ppm

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6.82 6.82 6.76 6.75 5.94 4.11 3.60 2.61 2.59 2.56 2.05 1.74 1.72 1.69 1.38 0.90

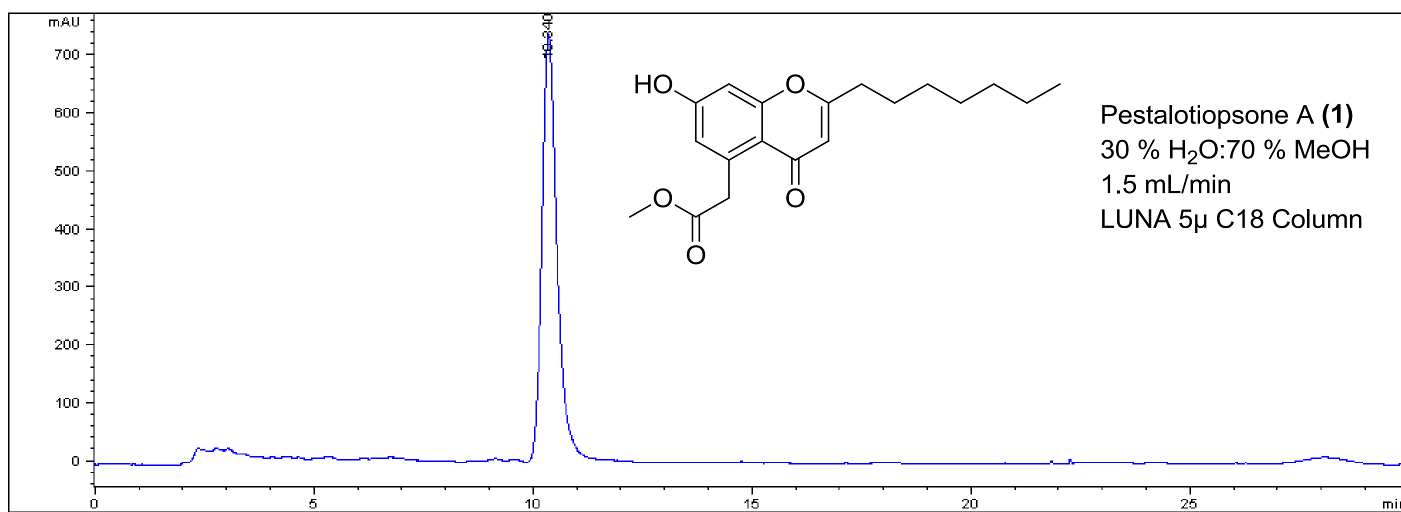
Pestalotiopsone F (4)
^{1}H NMR
300 MHz
acetone-d_6

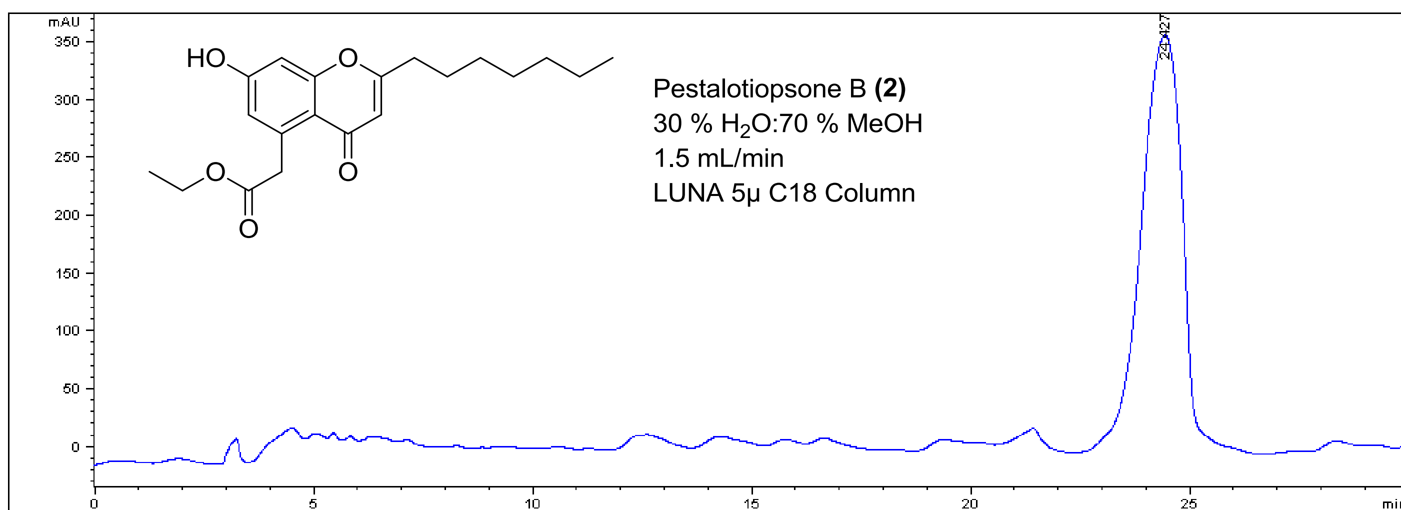
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

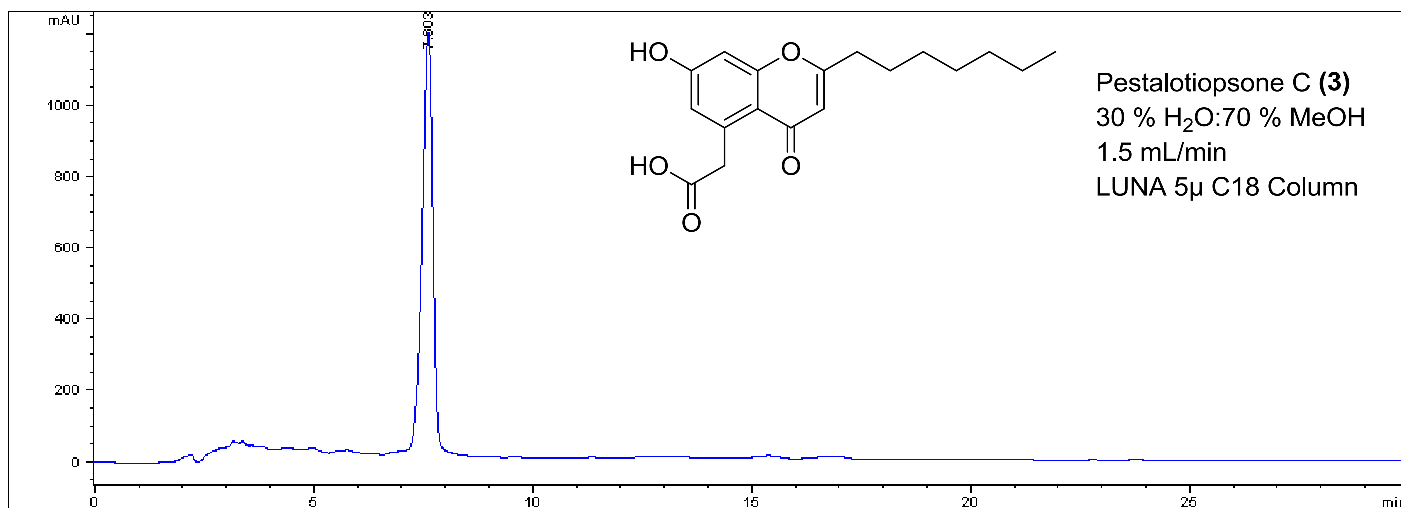
179.10 171.85 168.41 161.71 160.36 138.76 118.56 116.11 110.79 102.71 51.58 40.94 29.84 29.84 27.12 22.99 14.19

Pestalotiopsone F (4)
^{13}C NMR
75 MHz
acetone-d_6

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm


Pestalotiopsone A (1)
30 % H_2O:70 % MeOH
1.5 mL/min
LUNA 5μ C18 Column
mAU
10.340
min


Pestalotiopsone B (2)
30 % H_2O:70 % MeOH
1.5 mL/min
LUNA 5μ C18 Column
mAU
24.427
min


Pestalotiopsone C (3)
30 % H_2O:70 % MeOH
1.5 mL/min
LUNA 5μ C18 Column
mAU
7.603
min

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