Supporting Information

The formation of sesquiterpenoid presilphiperfolane and cameroonane metabolites in the BcBot4 null mutant of Botrytis cinerea.

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Table S1. NMR Spectroscopic data of presilphiperfolan-8α,10β,14-triol (16) (1H at 500 MHz, 13C at 125 MHz).

| Position | Proton | δ_1H (Hz) | δ_13C | NOESY | HMBC |
|----------|--------|-----------|-------|--------|------|
| 1        | H-1α   | 1.45 (1H, m) | 44.9  | H-2β, H-3α | C-2, C-9, C-10, C-11, C-15 |
| 2        | H-2α   | 1.94 (1H, m) | 34.3  | H-2α, H-3β, H-9β | C-1, C-3, C-9, C-10, C-11 |
|          | H-2β   | 2.36 (1H, m) |       |        |      |
| 3        | H-3α   | 1.94 (1H, m) | 34.1  | H-2α, H-3β | C-1, C-3 |
|          | H-3β   | 1.15 (1H, m) |       |        | C-4, C-8, C-12 |
| 4        | -      | -          | 57.9  | -      |      |
| 5        | H-5α   | 2.04 (1H, d, J=12.1 Hz) | 43.5  | H-5β, H-14 | C-3, C-4, C-6, C-12, C-13, C-14, C-15 |
|          | H-5β   | 1.03 (1H, d, J=12.1 Hz) |       | H-5α, H-12, H-13 | C-4, C-6, C-7, C-8, C-12, C-13 |
| 6        | -      | -          | 54.4  | -      |      |
| 7        | H-7α   | 1.88 (1H, m) | 45.9  | H-11α, H-14 | C-4, C-6, C-8, C-10, C-11, C-13, C-14 |
| 8        | -      | -          | 95.3  | -      |      |
| 9        | H-9β   | 1.43 (1H, m) | 47.6  | -      |      |
| 10       | H-10α  | 3.25 (1H, ddd, J=11, 9.4, 3.4, Hz) | 76.3  | H-7α, H-15 | C-7, C-9, C-11, C-15 |
| 11       | H-11α  | 1.84 (1H, m) | 36.9  | H-12, H-13 | C-6, C-7, C-8, C-10 |
|          | H-11β  | 1.61 (1H, ddd, J = 12, 11 Hz) |       |        |      |
| 12       | H-12   | 1.36 (3H, s) | 29.0  | H-13 | C-3, C-4, C-5, C-8 |
| 13       | H-13   | 1.18 (3H, s) | 22.8  | H-12 | C-5, C-6, C-7, C-14 |
| 14       | H-14   | 3.35 (2H, d superimposed, J = 10 Hz) | 72.5  | H-5α, H-7α | C-5, C-6, C-7, C-13 |
| 15       | H-15   | 0.99 (3H, d, J = 5.9 Hz) | 18.0  | H-1α, H-10α, H-14 | C-1, C-9, C-10, C-11 |

S2
Table S2. NMR Spectroscopic data of 8α,14-dihydroxypresilphiperfolan-10-one (17) (\(^1\)H at 600 MHz, \(^{13}\)C at 150 MHz).

| Position | Proton | \(\delta^1\)H (Hz) | \(\delta^{13}\)C | NOESY | HMBC |
|----------|--------|------------------|-----------------|-------|------|
| 1        | H-1\(\alpha\) | 1.71 (1H, m)     | 48.09           |       |      |
| 2        | H-2    | 2.05 (1H, m)     | 34.9            |       |      |
|          | H-2'   | 2.50 (1H, m)     |                 |       |      |
| 3        | H-3    | 1.98 (1H, m)     | 32.7            |       |      |
|          | H-3'   | 1.26 (1H, m)     |                 |       |      |
| 4        | -      |                  | 57.8            |       |      |
| 5        | H-5\(\alpha\) | 2.17 (1H, d, \(J = 12.1\) Hz) | 41.7 |       |      |
|          | H-5\(\beta\) | 1.14 (1H, d, \(J = 12.1\) Hz) |             | H-13  |      |
| 6        | -      |                  | 54.0            |       |      |
| 7        | H-7\(\alpha\) | 2.20 (1H, m) | 46.2  |       |      |
| 8        | -      |                  | 92.4            |       |      |
| 9        | H-9\(\beta\) | 2.43 (1H, dq, \(J = 12.4, 6.3\) Hz) | 48.13 |       |      |
| 10       | H-10   |                  | 213.7           |       |      |
| 11       | H-11\(\alpha\) | 2.34 (1H, dd, \(J = 13.1, 8.7\) Hz) | 42.2 |       |      |
|          | H-11\(\beta\) | 2.52 (1H, dd, \(J = 13.1\) Hz) |              | H-11, H-2\(\beta\) | C-7, C-9, C-8, C-10 |
| 12       | H-12   | 1.54 (3H, s)     | 28.14           |       |      |
| 13       | H-13   | 1.14 (3H, s)     | 22.5            |       |      |
| 14       | H-14   | 3.44 (2H, s(br)) | 71.5           | H-13  |      |
| 15       | H-15   | 0.98 (3H, d, \(J = 6.4\) Hz) | 13.5 |       |      |
| Position | Proton | $\delta^1H$ (Hz) | $\delta^{13}C$ | NOESY | HMBC |
|----------|--------|----------------|-------------|------|------|
| 1        |        |                | 148.7       |      |      |
| 2        | H-2    | 4.94 (1H, dd, $J = 2.5, 2.1$ Hz) | 116.2 | C-3, C-4, C-8 |
| 3        | H-3    | 2.40 (1H, dd, $J = 17, 2.1$ Hz) | 50.25 | C-1, C-2, C-4, C-8, C-12 |
|          | H-3'   | 2.25 (1H, dt, $J = 17, 2.5$, Hz) | | C-1, C-2, C-4, C-5, C-12 |
| 4        |        |                | 47.1        |      |      |
| 5        | H-5    | 1.87 (1H, d, $J = 13.3$ Hz) | 53.43 | C-3, C-6, C-12, C-13, C-14 |
|          | H-5'   | 1.56 (1H, d, $J = 13.3$ Hz) | |      |
| 6        |        |                | 46.4        |      |      |
| 7        | H-7\(\alpha\) | 1.36 (1H, m) | 53.4 | C-6, C-8, C-11, C-13 |
| 8        |        |                | 93.5        |      |      |
| 9        | H-9\(\beta\) | 2.46 (1H, m) | 39.7 |      |
| 10       | H-10   | 3.18 (1H, ddd, $J = 10, 8.7, 5.3$ Hz) | 79.8 | C-15 |
| 11       | H-11   | 1.94 (1H, m) | 30.5 | C-7, C-8, C-10 |
|          | H-11'  | 1.86 (1H, m) | | C-7, C-8, C-9, C-10 |
| 12       | H-12   | 1.11 (3H, s) | 29.7 | C-3, C-4, C-5, C-8 |
| 13       | H-13   | 1.07 (3H, s) | 18.9 | C-5, C-6, C-14 |
| 14       | H-14   | 3.33 (2H, d(br), $J = 4$ Hz) | 71.0 | C-5, C-6, C-13 |
| 15       | H-15   | 1.20 (3H, d, $J = 6.5$ Hz) | 14.15 | C-1, C-9, C-10 |
Table S4. NMR Spectroscopic Data of cameroonan-7α, 10β, 14-triol (19) (\(^1\)H at 500 MHz, \(^{13}\)C at 125 MHz).

| Position | Proton    | \(\delta_{\text{H}}\) (Hz)                          | \(\delta_{\text{C}}\) | NOESY                  | HMBC                        |
|----------|-----------|----------------------------------------------------|------------------------|-------------------------|-----------------------------|
| 1        | H-1α      | 2.17 (1H, t, \(J = 9.0\) Hz)                      | 47.85                  | H-14, H-15              | C-2, C-4, C-7, C-8, C-9, C-11, C-13, C-15 |
| 2        | H-2       | 1.34 (1H, m)                                       | 28.62                  |                         | C-4, C-8, C-9               |
|          | H-2’      | 1.80 (1H, m)                                       | 38.93                  |                         | C-1, C-3, C-9               |
| 3        | H-3       | 1.49 (2H, m)                                       |                        |                         | C-2, C-4, C-12              |
|          | H-3’      | -                                                  | 48.47                  |                         |                             |
| 4        | -         | -                                                  | 48.47                  |                         |                             |
| 5        | H-5       | 1.27 (1H, d superimposed)                          | 47.42                  |                         | C-3, C-4, C-6, C-7, C-8, C-12, C-13, C-14 |
|          | H-5’      | 1.39 (1H, d \(J = 14.5\) Hz)                      | 47.42                  |                         | C-3, C-4, C-6, C-7, C-12, C-13, C-14 |
| 6        | -         | -                                                  | 42.35                  |                         |                             |
| 7        | H-7β      | 3.89 (1H, s)                                       | 91.52                  | H-9β, H-11b, H-12       | C-1, C-6, C-8, C-11, C-14, C-13 |
| 8        | -         | -                                                  | 62.85                  |                         |                             |
| 9        | H-9β      | 1.22 (1H, m)                                       | 49.96                  |                         |                             |
| 10       | H-10α     | 3.72 (1H, ddd, \(J = 11, 9.7, 6.0\) Hz)           | 77.45                  | H-11a, H-11b, H-15      | C-9, C-15                   |
| 11       | H-11      | 1.65 (1H,dd, 12.2, 11 Hz)                          | 44.83                  | H-10α                   | C-4, C-7, C-8, C-10         |
|          | H-11’     | 1.73 (1H, dd, \(J = 12.2, 6\) Hz)                 |                        | H-7β, H-10α             | C-1, C-7, C-8, C-9          |
| 12       | H-12      | 1.00 (3H, s)                                       | 25.03                  | H-9β, H-11a, H-3        | C-1, C-3, C-8               |
| 13       | H-13      | 1.20 (3H, s)                                       | 27.39                  | H-7β, H-14α             | C-5, C-6, C-7, C-14         |
| 14       | H-14      | 3.21 (1H, d, \(J = 10.9\) Hz)                     | 69.61                  | H-9β, H-5, H-14b        | C-5, C-6, C-7, C-13         |
|          | H-14’     | 3.82 (1H, d, \(J = 10.9\) Hz)                     |                        | H-1, H-5, H-2, H-14a    | C-5, C-6, C-7, C-13         |
| 15       | H-15      | 1.05 (3H, d, \(J = 6.5\) Hz)                      | 16.36                  | H-1α, H-10α             | C-1, C-9, C-10              |
Table S5. NMR Spectroscopic Data of cameroonan-2α, 3β, 7α-triol (20) \((^1\text{H at 500 MHz, } ^{13}\text{C at 125 MHz})\).

| Position | Proton | δ_H (Hz) | δ^{13}C | NOESY | HMBC |
|----------|--------|----------|---------|--------|------|
| 1        | H-1α   | 2.10 (1H, dd, \(J = 8.6, 3.7 \text{ Hz}\)) | 54.8    |        | C-2, C-7, C-8, C-11, C-15 |
| 2        | H-2β   | 3.49 (1H, dd, \(J = 9.1, 8.6 \text{ Hz}\)) | 82.9    | H-12, H-9 | C-3, C-9 |
| 3        | H-3α   | 3.81 (1H, db, \(J = 9.1 \text{ Hz}\)) | 86.5    | H-1, H-5α, H-14 | C-2, C-5, C-12 |
| 4        | -      |          | 49.8    |        |      |
| 5        | H-5α   | 1.83 (1H, d, \(J = 13.5 \text{ Hz}\)) | 52.85   | H-5β, H-3 | C-7, C-3, C-8, C-4, C-6, C-13, C-14, C-12 |
|          | H-5β   | 1.29 (1H, d, \(J = 13.5 \text{ Hz}\)) |         |        | C-7, C-3, C-8, C-4, C-6, C-13, C-14, C-12 |
| 6        | -      |          | 43.7    |        |      |
| 7        | H-7β   | 3.33 (1H, s) | 90.4    | H-11β, H-13 | C-4, C-5, C-11, C-13, C-14 |
| 8        | -      |          | 64.10   | H-10, H-11, H-12 |      |
| 9        | H-9β   | 1.94 (1H, m) | 38.61   |        | C-2, C-8, C-11, C-15 |
| 10       | H-10α  | 1.34 (1H, m) | 34.9    |        | C-1, C-8, C-9, C-11, C-15 |
|          | H-10β  | 1.73 (1H, m) |         |        | C-1, C-8, C-9, C-11, C-15 |
| 11       | H-11α  | 1.90 (1H, m) | 35.7    |        | C-10, C-9, C-7, C-4, C-1 |
|          | H-11β  | 1.55 (1H, m) |         |        | C-10, C-9, C-7, C-4, C-1 |
| 12       | H-12   | 0.95 (3H, s) | 20.0    |        | C-4, C-5, C-8, C-3 |
| 13       | H-13   | 1.03 (3H, s) | 29.4    |        | C-5, C-6, C-7, C-14 |
| 14       | H-14   | 1.03 (3H, s) | 24.3    |        | C-5, C-6, C-7, C-13 |
| 15       | H-15   | 1.01 (1H, d, \(J = 6.9 \text{ Hz}\)) | 20.3    | H-1, H-10α | C-10, C-9, C-1 |

S6
Table S6. NMR Spectroscopic Data of 7-α-hydroxycameroonan-14,15-dioic acid 14-7-lactone (21) (¹H at 500 MHz, ¹³C at 125 MHz).

| Position | Proton | \( \delta_\text{H} \) (Hz) | \( \delta_\text{C} \) | NOESY | HMBC |
|----------|--------|------------------|-------------|-------|------|
| 1        | H-1α   | 3.01 (1H, dt, J 6.7, 8.3 Hz) | 50.71       |       | C-2, C-4, C-7, C-8, C-9, C-11, C-15 |
| 2        | H-2    | 1.52 (1H, m)       | 32.50       |       | C-1, C-3, C-9 |
|          | H-2’   | 2.14 (overlap)     |             |       |      |
| 3        | H-3α   | 1.90 (1H, m)       | 42.63       |       | C-2, C-4, C-5, C-12 |
|          | H-3β   | 1.64 (1H, dd, J 12.7, 6.7 Hz) | 42.63 |       | C-1, C-2, C-4, C-8, C-12 |
| 4        | -      | -                 | 54.83       |       |      |
| 5        | H-5α   | 2.28 (1H, d, J 14.4 Hz) | 45.09       | H-12, H-13 | C-3, C-4, C-6, C-8, C-14 |
|          | H-5β   | 1.37 (1H, d, J 14.4 Hz) | 45.09       |       |      |
| 6        | -      | -                 | 62.26       |       |      |
| 7        | H-7β   | 4.27 (1H, s)       | 93.64       | H-13  | C-4, C-5, C-8, C-11, C-13, C-14 |
| 8        | -      | -                 | 65.33       |       |      |
| 9        | H-9β   | 2.52 (1H, dt, J 6.7, 8.3 Hz) | 51.66 | H-10β | C-1, C-2, C-8, C-10, C-11, C-15 |
| 10       | H-10α  | 2.14 (overlap)     | 32.95       |       |      |
|          | H-10β  | 2.04 (1H, m)       | 32.95       |       | C-1, C-8, C-9, C-11, C-15 |
| 11       | H-11α  | 1.44 (1H, dd, J 13.2, 6.4 Hz) | 31.12 |       | C-1, C-4, C-7, C-8, C-9, C-10 |
|          | H-11β  | 1.80 (1H, m)       | 31.12       |       | C-4, C-7, C-8, C-9, C-10 |
| 12       | H-12   | 1.07 (3H, s)       | 25.14       | H-3β, H-5β, H-11β | C-3, C-4, C-5, C-8 |
| 13       | H-13   | 1.40 (3H, s)       | 18.00       | H-5β, H-7β | C-5, C-6, C-7, C-14 |
| 14       | -      | -                 | 175.74      |       |      |
| 15       | -      | -                 | 180.62      |       |      |
$^1$H-NMR spectrum of presilphiperfolan-8α,10β,14-triol (16) (CD$_3$OD at 500 MHz).
$^{13}$C-NMR spectrum of presilphiperfolan-8α,10β,14-triol (16) (CD$_3$ OD, at 125 MHz).
$^1$H-NMR spectrum of 10β,14-Diacetoxyresilphiperfolan-8α-ol (16a) (CDCl$_3$ at 500 MHz).
$^{13}$C-NMR spectrum of 10β,14-Diacetoxypresilphiperfolan-8α-ol (16a) (CDCl$_3$ at 125 MHz).
$^1$H-NMR spectrum of 8α,14-dihydroxypresilphiperfolan-10-one (17) (CDCl$_3$ at 600 MHz).
$^{13}$C-NMR spectrum of 8α,14-dihydroxypresilphiperfolan-10-one (17) (CDCl$_3$ at 150 MHz).
$^1$H-NMR spectrum of $8\alpha,10\beta,14$-trihydroxypresilphiperfol-1-ene (18) (CDCl$_3$ at 600 MHz).
$^{13}$C-NMR spectrum of 8α,10β,14-trihydroxyresilphiperfol-1-ene (18) (CDCl$_3$ at 150 MHz).
$^1$H-NMR spectrum of cameroonan-7α,10β,14-triol (19) (CDCl$_3$ at 500 MHz).
$^{13}$C-NMR spectrum of cameroonan-7α,10β,14-triol (19) (CDCl$_3$ at 125 MHz).
$^1$H-NMR spectrum of 7α, 10β, 14-triacetoxycameroonane (19a) (CDCl$_3$ at 500 MHz).
$^{13}$C-NMR spectrum of 7α, 10β, 14-triacetoxycameroonane (19a) ($CDCl_3$ at 125 MHz).
$^1$H-NMR spectrum of cameroonan-2α, 3β, 7α-triol (20) (CDCl$_3$ at 500 MHz).
$^{13}$C-NMR spectrum of cameroonan-2α, 3β, 7α-triol (20) (CDCl$_3$ at 125 MHz).
$^1$H-NMR spectrum of 2α, 3β, 7α-triacetoxycameroonane (20a) (CDCl$_3$ at 400 MHz).
$^{13}$C-NMR spectrum of 2α, 3β, 7α-triacetoxycameroonane (20a) (CDCl$_3$ at 100 MHz).
$^1$H-NMR spectrum of 7-α-hydroxycameroonan-14,15-dioic acid 14-7-lactone (21) (CDCl$_3$ at 500 MHz).
$^{13}$C-NMR spectrum of 7-α-hydroxycameroonan-14,15-dioic acid 14-7-lactone (21) (CDCl$_3$ at 500 MHz).