Chemical constituents of the egg cases of *Tenodera angustipennis* (Mantidis ootheca) with intracellular reactive oxygen species scavenging activity

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Figure S1: Structures of known compounds (3–15)
Figure S2: Spectroscopic data of known compounds (3–14)

N-acetyldopamine (3): ESIMS (positive) m/z 196 [M + H]⁺; ESIMS (negative) m/z 194 [M – H]⁻; ¹H NMR (CD₃OD, 500 MHz) δ 6.68 (1H, d, J = 8.1 Hz, H-5), 6.64 (1H, d, J = 2.1 Hz, H-2), 6.52 (1H, dd, J = 8.0, 2.1 Hz, H-6), 3.31 (2H, overlap with MeOD, H-8), 2.62 (2H, t, J = 7.4 Hz, H-7), 1.90 (3H, s, H-10); ¹³C NMR (CD₃OD, 125 MHz) δ 173.4 (C-9), 146.4 (C-3), 144.9 (C-4), 132.2 (C-1), 121.2 (C-6), 117.0 (C-2), 116.5 (C-5), 42.6 (C-8), 36.0 (C-7), 22.7 (C-10).

2-oxo-N-acetyldopamine (4): ESIMS (positive) m/z 210 [M + H]⁺; ESIMS (negative) m/z 208 [M – H]⁻; ¹H NMR (CD₃OD, 500 MHz) δ 7.45 (1H, d, J = 8.7 Hz, H-6), 7.42 (1H, s, H-2), 6.84 (1H, d, J = 8.2 Hz, H-5), 4.60 (2H, s, H-8), 2.05 (3H, s, H-10); ¹³C NMR (CD₃OD, 125 MHz) δ 194.9 (C-7), 173.9 (C-9), 152.8 (C-4), 146.8 (C-3), 128.7 (C-1), 122.9 (C-6), 116.2 (C-5), 115.8 (C-2), 46.9 (C-8), 22.6 (C-10).

4-hydroxybenzaldehyde (5): ESIMS (positive) m/z 123 [M + H]⁺; ESIMS (negative) m/z 121 [M – H]⁻; ¹H NMR (CD₃OD, 500 MHz) δ 9.79 (1H, s, H-7), 7.80 (2H, d, J = 8.7 Hz, H-2 and H-6), 6.94 (2H, d, J = 8.5 Hz, H-3 and H-5); ¹³C NMR (CD₃OD, 125 MHz) δ 193.0 (C-7), 165.4 (C-4), 133.6 (C-2 and C-6), 130.5 (C-1), 117.0 (C-3 and C-5).

4-hydroxybenzoic acid (6): ESIMS (positive) m/z 139 [M + H]⁺; ESIMS (negative) m/z 137 [M – H]⁻; ¹H NMR (CD₃OD, 500 MHz) δ 7.87 (2H, d, J = 8.4 Hz, H-2 and H-6), 6.82 (2H, d, J = 8.1 Hz, H-3 and H-5); ¹³C NMR (CD₃OD, 125 MHz) δ 169.8 (C-7), 163.5 (C-4), 133.3 (C-2 and C-6), 123.7 (C-1), 116.2 (C-3 and C-5).
Apocynin (7): ESIMS (positive) m/z 167 [M + H]^+; ESIMS (negative) m/z 165 [M – H]^−; 1H NMR (CD$_3$OD, 500 MHz) δ 7.56 (1H, dd, J = 8.5, 2.1 Hz, H-6), 7.42 (1H, s, H-2), 7.02 (1H, d, J = 8.4 Hz, H-5), 3.94 (3H, s, OCH$_3$-3); 13C NMR (CD$_3$OD, 125 MHz) δ 199.7 (C-7), 153.8 (C-4), 147.7 (C-3), 131.7 (C-1), 123.2 (C-6), 115.7 (C-5), 111.7 (C-2), 56.5 (OCH$_3$-3), 26.4 (C-8).

Benzoic acid (8): ESIMS (negative) m/z 121 [M – H]^−; 1H NMR (CD$_3$OD, 500 MHz) δ 8.01 (2H, d, J = 8.0 Hz, H-2 and H-6), 7.57 (1H, t, J = 7.4 Hz, H-4), 7.46 (1H, t, J = 7.5 Hz, H-3 and H-5); 13C NMR (CD$_3$OD, 125 MHz) δ 170.1 (C-7), 133.9 (C-2 and C-6), 131.2 (C-4), 130.6 (C-1), 129.6 (C-3 and C-5).

Protocatechuic acid (9): ESIMS (positive) m/z 155 [M + H]^+; ESIMS (negative) m/z 153 [M – H]^−; 1H NMR (CD$_3$OD, 500 MHz) δ 7.42 (2H, overlap with H-2 and H-6), 6.79 (1H, d, J = 7.9 Hz, H-5); 13C NMR (CD$_3$OD, 125 MHz) δ 170.6 (C-7), 151.6 (C-4), 146.2 (C-3), 124.1 (overlap, C-1 and C-6), 117.9 (C-2), 115.9 (C-5).

4-hydroxyphenylacetic acid (10): ESIMS (negative) m/z 151 [M – H]^−; 1H NMR (CD$_3$OD, 500 MHz) δ 7.08 (2H, d, J = 8.3 Hz, H-2 and H-6), 6.72 (2H, d, J = 8.5 Hz, H-3 and H-5), 3.50 (2H, s, H-7); 13C NMR (CD$_3$OD, 125 MHz) δ 176.2 (C-8), 157.6 (C-4), 146.2 (C-3), 124.1 (overlap, C-1 and C-6), 127.1 (C-1), 116.3 (C-3 and C-5), 41.7 (C-7).

(S)-1-phenylethane-1,2-diol (11): [α]$^{26}_D +10.8$ (c 0.01, MeOH); ESIMS (positive) m/z 139 [M + H]^+; ESIMS (negative) m/z 137 [M – H]^−; 1H NMR (CD$_3$OD, 500 MHz) δ 7.37 (2H, d, J = 7.1 Hz, H-2 and H-6), 7.33 (2H, t, J = 7.5 Hz, H-3 and H-5), 7.25 (1H, t, J = 7.3 Hz, H-4), 4.68 (1H, t, J = 5.5 Hz, H-7), 3.60 (2H, overlap with MeOH, H-8); 13C NMR (CD$_3$OD, 125 MHz) δ 143.5 (C-1), 129.4 (C-3 and C-5), 128.7 (C-4), 127.6 (C-6), 76.1 (C-7), 68.9 (C-8).
4-hydroxyphenylglyoxylic acid amide (12): ESIMS (negative) \( m/z \) 164 \([M - H]^−\); \(^1\)H NMR (CD\(_3\)OD, 500 MHz) \( \delta \) 8.01 (2H, \( d, J = 8.8 \text{ Hz}, \text{H-2 and H-6} \)), 6.87 (2H, \( d, J = 8.9 \text{ Hz}, \text{H-3 and H-5} \)); \(^{13}\)C NMR (CD\(_3\)OD, 125 MHz) \( \delta \) 189.8 (C-7), 170.2 (C-8), 165.4 (C-3), 134.3 (C-2 and C-6), 126.1 (C-1), 116.7 (C-3 and C-5).

(±)-hydroxybutenolide (13): Racemic mixture, ESIMS (positive) \( m/z \) 193 \([M + H]^+\); ESIMS (negative) \( m/z \) 191 \([M - H]^−\); \(^1\)H NMR (CD\(_3\)OD, 500 MHz) \( \delta \) 7.67 (2H, \( d, J = 8.8 \text{ Hz}, \text{H-2 and H-6} \)), 6.86 (2H, \( d, J = 8.8 \text{ Hz}, \text{H-3 and H-5} \)), 6.50 (1H, s, H-2’), 6.32 (1H, s, H-4’); \(^{13}\)C NMR (CD\(_3\)OD, 125 MHz) \( \delta \) 174.3 (C-5’), 165.8 (C-3’), 162.3 (C-4), 131.5 (C-2 and C-6), 122.4 (C-1), 117.0 (C-3 and C-5), 111.9 (C-4’), 100.1 (C-2’).

Scoparone (14): ESIMS (positive) \( m/z \) 207 \([M + H]^+\); \(^1\)H NMR (CD\(_3\)OD, 500 MHz) \( \delta \) 7.90 (1H, \( d, J = 9.4 \text{ Hz}, \text{H-4} \)), 7.15 (1H, s, H-5), 7.00 (1H, s, H-8), 6.27 (1H, \( d, J = 9.4 \text{ Hz}, \text{H-3} \)), 3.93 (3H, s, OCH\(_3\)-7), 3.88 (3H, s, OCH\(_3\)-6); \(^{13}\)C NMR (CD\(_3\)OD, 125 MHz) \( \delta \) 164.0 (C-2), 155.0 (C-7), 151.5 (C-8a), 148.3 (C-6), 146.1 (C-4), 113.7 (C-3), 113.3 (C-4a), 110.1 (C-5), 101.2 (C-8), 57.0 (OCH\(_3\)-7), 57.0 (OCH\(_3\)-6).
Figure S3: GC-MS spectrum of compound 15
Figure S4: $^1$H NMR spectrum of tenoderin A (1) (CD$_3$OD, 500 MHz)
Figure S5: $^{13}$C NMR spectrum of tenoderin A (1) (CD$_3$OD, 125 MHz)
Figure S6: HSQC NMR spectrum of tenoderin A (1) (CD$_3$OD)
Figure S7: HMBC NMR spectrum of tenoderin A (1) (CD$_3$OD)
Figure S8: COSY NMR spectrum of tenoderin A (I) (CD$_3$OD)
Figure S9: HRESIMS spectrum of tenoderin A (1) (CD$_3$OD)

Elemental Composition Report

Tolerance = 5.0 PPM  /  DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1273 formula(e) evaluated with 9 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-500  H: 0-1000  N: 0-200  O: 0-200
200805_SeohYH_SM-S6-1K_Neg (0.026) Is (1.00,1.00) C20H22N2O7
1. TOF MS ES-

| Mass   | RA    | Calc. Mass | mDa  | PPM  | DBE | i-FIT | Norm | Conf(%) | Formula |
|--------|-------|------------|------|------|-----|-------|------|---------|---------|
| 401.1349 | 100.00 | 401.1349 | 0.0  | 0.0  | 11.5 | 46.9  | 0.000 | 100.00  | C20 H21 N2 O7 |
| 401.1362 | -1.3  | -3.2     | 16.5 | 70.9 | 23.914 | 0.00 | C21 H17 N6 O3 |
| 401.1355 | 1.4  | 3.5     | 17.5 | 75.1 | 28.125 | 0.00 | C17 H13 N12 O |
| 401.1330 | 1.9  | 4.7     | 24.5 | 79.1 | 32.116 | 0.00 | C32 H17 |
| 401.1367 | -1.8  | -4.5 | -1.5 | 79.4 | 32.480 | 0.00 | C8 H25 N4 O14 |
| 401.1354 | -0.5  | -1.2 | 4.5 | 82.4 | 35.444 | 0.00 | C5 H17 N14 O8 |
| 401.1367 | -1.8  | -4.5 | 9.5 | 82.6 | 35.612 | 0.00 | C6 H13 N18 O4 |
| 401.1340 | 0.9  | 2.2     | 10.5 | 86.1 | 39.154 | 0.00 | C2 H9 N24 O2 |
Figure S10: $^1$H NMR spectrum of tenoderin B (2) (CD$_3$OH, 500 MHz)
Figure S11: $^{13}$C NMR spectrum of tenoderin B (2) (CD$_3$OH, 125 MHz)
Figure S12: HSQC NMR spectrum of tenoderin B (2) (CD$_3$OH)
Figure S13: HMBC NMR spectrum of tenoderin B (2) (CD$_3$OH)
Figure S14: COSY NMR spectrum of tenoderin B (2) (CD$_3$OH)
Figure S15: HRESIMS spectrum of tenoderin B (2)

**Elemental Composition Report**

**Multiple Mass Analysis: 2 mass(es) processed**
- Tolerance = 5.0 PPM
- DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
659 formula(e) evaluated with 4 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:
- C: 0-500
- H: 0-1000
- N: 0-200
- O: 0-200

202805_SeoYH_SM-36-1K_Neg-re 326 (3.701) Cm (320:331)
1: TOF MS ES-

| Mass  | RA   | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula     |
|-------|------|------------|-----|-----|-----|-------|------|---------|-------------|
| 314.1042 | 100.00 | 314.1042 | 0.0 | 15.5 | 1134.2 | 0.060 | 94.20 | C18 H12 N5 O |
| 314.1028 | 1.4   | 314.1028  | 1.6 | 5.79 | 1137.0 | 2.848 | C17 H16 N O5 |
| 314.1047 | -0.5  | 314.1047  | -1.6| 8.5  | 1143.9 | 9.758 | 0.01 | C3 H8 N17 O2 |
| 314.1034 | 0.8   | 314.1034  | 3.5 | 1144.3 | 10.142 | 0.00 | C2 H12 N13 O6 |
Figure S16: Stereomicroscope micrographs showing the ootheca morphology of *Tenodera angustipennis*. (A) Dorsal view; (B) Lateral view; (C) Surface pattern on lateral view; Scale bars = 1 cm (A, B). 1 mm (C)
Table S1: Screening of the antioxidant activity of extract (100 µg/mL) and isolated compounds (100 µM)

| Compounds | Antioxidant capacity (%) |      |      |
|-----------|--------------------------|------|------|
|           |                          | DPPH | ABTS |
| Extract   | 81.99 ± 1.98 1)          |      | 99.74 ± 0.13 |
| 1         | 56.59 ± 0.60             | 60.56 ± 0.18 |
| 1b        | 71.16 ± 0.22             | 67.77 ± 1.29 |
| 2         | 80.83 ± 0.09             | 93.13 ± 0.31 |
| 3         | 76.39 ± 2.60             | 95.87 ± 0.12 |
| 4         | 81.93 ± 0.25             | 89.53 ± 0.17 |
| 5         | -1.83 ± 0.75             | 0.93 ± 1.46  |
| 6         | 0.37 ± 0.28              | -0.12 ± 0.99 |
| 7         | 9.40 ± 0.97              | 1.59 ± 1.23  |
| 8         | -1.00 ± 0.52             | 1.39 ± 1.27  |
| 9         | 78.87 ± 0.48             | 92.38 ± 0.04 |
| 10        | 38.80 ± 1.09             | 11.45 ± 0.86 |
| 11        | 41.58 ± 0.90             | 19.05 ± 0.48 |
| 12        | -0.53 ± 1.40             | 2.06 ± 0.69  |
| 13        | -0.03 ± 1.58             | 0.37 ± 0.12  |
| 14        | -1.74 ± 1.70             | 0.37 ± 0.26  |
| 15        | -2.40 ± 1.42             | -1.79 ± 0.45 |
| Gallic acid | 82.89 ± 0.09           |      | 95.40 ± 0.07 |

1) Values are reported as mean ± SD (n=3)