

Supplementary Materials

Table S1. NMR data for compounds **3** and **4**.

| | 3 (PC B3) | | 4 (PC B4) | | |
|------------|--|---|--|---|---|
| | $\delta_{C, \text{major}} + \delta_{C, \text{minor}}$ type | $\delta_{H, \text{major}}$ (<i>J</i> in Hz) + $\delta_{H, \text{minor}}$ (<i>J</i> in Hz) | $\delta_{C, \text{major}} + \delta_{C, \text{minor}}$ type | $\delta_{H, \text{major}}$ (<i>J</i> in Hz) + $\delta_{H, \text{minor}}$ (<i>J</i> in Hz) | |
| | 2 | 84.0 + 84.1, CH | 4.25, d (9.7) + 4.35, d (9.1) | 83.9 + 84.1, CH | 4.41, d (9.7) + 4.31 ⁱ , m |
| | 3 | 73.7 ^a + 73.7 ^a , CH | 4.35, dd (9.7, 8.0) + 4.51, d (9.1) | 73.8 + 73.8, CH | 4.56, d (8.0) + 4.31 ⁱ , m |
| | 4 | 38.6 + 38.5, CH | 4.40, d (7.9) + 4.49, d (8.0) | 38.9 + 38.8, CH | 4.62, d (7.9) + 4.46, d (7.1) |
| | 4a | 107.2 + 107.1, C | | 107.2 + 107.4, C | |
| | 5 | 157.1 ^b , C | | 157.5 + 157.2, C | |
| | 6 | 97.3 + 97.5, C | 5.88, d (2.4) + 5.80, d (2.3) | 97.6 + 97.7, CH | 5.79, d (2.1) + 5.89, d (2.1) |
| Upper unit | 7 | 157.1 ^b + 157.3, C | | 157.3 + 157.3, C | |
| | 8 | 96.9 + 96.2, CH | 5.78, d (2.4) + 5.83, d (2.4) | 96.1 + 97.1, CH | 5.83, d (2.3) + 5.93, d (2.2) |
| | 8a | 158.6, C | | 158.7 + 158.6, C | |
| | 1' | 132.6 + 132.4, C | | 132.2 + 132.6, C | |
| | 2' | 116.4 + 116.2 ^c , CH | 6.73, d (1.9) + 6.95, d (1.9) | 116.3 + 116.4, CH | 6.98, d (1.9) + 6.69, d (1.9) |
| | 3' | 145.6 + 146.1 ^d , C | | 146.5 + 145.6, C | |
| | 4' | 146.1 + 146.1, C | | 146.0 + 146.1, C | |
| | 5' | 116.2 + 115.9, CH | 6.66, d (8.1) + 6.76, d (8.0) | 116.0 ^f + 116.1 ^f , CH | 6.79 ^j , d (7.7) + 6.60, d (8.2) |
| | 6' | 120.6 + 121.0, CH | 6.46, dd (8.2, 1.9) + 6.81 ^e , dd (8.0, 1.9) | 121.2 + 120.5, CH | 6.86, d (8.0) + 6.41, dd (8.2, 1.8) |

Table S1. Cont.

| | 3 (PC B3) | | 4 (PC B4) | | |
|------------------|-----------|--|--|--|--|
| | Pos. | $\delta_{C, \text{major}} + \delta_{C, \text{minor}}$ type | $\delta_{H, \text{major}}$ (J in Hz) + $\delta_{H, \text{minor}}$ (J in Hz) | $\delta_{C, \text{major}} + \delta_{C, \text{minor}}$ type | $\delta_{H, \text{major}}$ (J in Hz) + $\delta_{H, \text{minor}}$ (J in Hz) |
| Terminal unit | 2 | 82.5 + 82.9, CH | 4.53, d (7.3) + 4.74, d (7.3) | 80.0 + 79.9, CH | 4.93, bs + 4.80, bs |
| | 3 | 68.9 + 68.6, CH | 3.78, m + 4.06, m | 67.4 + 67.8, CH | 4.22, m + 4.05, m |
| | 4 | 28.8 + 28.5, CH ₂ | 2.48, dd (16.2, 8.0) + 2.58, dd (16.1, 7.7) 2.75, dd (16.3, 5.5) + 2.81, dd (16.2, 5.4) | 30.1 + 29.4, CH ₂ | 2.82, dd (16.9, 1.7) + 2.70, dd (17.1, 2.3) 2.92, dd (16.8, 4.4) + 2.86, dd (17.0, 5.0) |
| | 4a | 102.2 + 100.5, C | | 99.4 + 101.5, C | |
| | 5 | 155.9 + 155.8, C | | 156.4 + 156.3, C | |
| | 6 | 96.1 + 97.5, C | 6.06, s + 5.93, s | 97.5 + 96.4, CH | 5.95, s + 6.09, s |
| | 7 | 155.7, C | | 155.9 ^g + 155.9 ^g , C | |
| | 8 | 108.2 + 108.3, C | | 108.7 + 108.3, C | |
| | 8a | 154.9 + 155.0, C | | 155.4 ^h + 155.4 ^h , C | |
| | 1' | 131.8 + 132.2, C | | 132.4 + 131.7, C | |
| | 2' | 115.5 + 115.2, CH | 6.58, d (1.9) + 6.95, d (1.9) | 115.3 + 114.8, CH | 7.08, d (1.6) + 6.67, d (1.8) |
| | 3' | 145.5 + 146.1 ^d , C | | 146.2 + 145.6, C | |
| | 4' | 145.8 + 146.1 ^d , C | | 145.7 + 145.6, C | |
| | 5' | 116.1 + 116.1 ^e , C | 6.67, d (8.2) + 6.75, d (8.2) | 116.1 + 115.9, CH | 6.77 ^j , d (8.2) + 6.71, d (8.2) |
| | 6' | 119.9 + 120.2, C | 6.25, dd (8.2, 1.9) + 6.82 ^e , dd (8.2, 1.8) | 119.1 + 120.3, CH | 6.86, d (8.0) + 6.44, dd (8.2, 1.8) |

^{a-j} Signals with the same letter are overlapped.

Table S2. NMR data for compounds **5** and **6**.

| | 5 (PC C1) | | | 6 (Epicatechin-β(4\rightarrow8)-epicatechin-β(4\rightarrow8)-catechin) | | | |
|-------------|------------------|-----------------------------|----------------------------------|---|-----------------------------|----------------------------------|----------------------------------|
| | Pos. | δ_C type (-40 °C) | δ_H (J in Hz) (-40 °C) | δ_H (J in Hz) (-20 °C) | δ_C type (-40 °C) | δ_H (J in Hz) (-40 °C) | δ_H (J in Hz) (-20 °C) |
| upper unit | 2 | 76.8, CH | 5.08, bs | 5.07, bs | 76.7, CH | 5.08 ^f , bs | 5.07, bs |
| | 3 | 73.5, CH | 3.95, d (1.9) | 3.97, d (1.9) | 73.5, CH | 3.98, d (1.6) | 3.99, d (1.8) |
| | 4 | 36.9, CH | 4.68, bs | 4.69, m | 36.8, CH | 4.67, bs | 4.68, bs |
| | 4a | 101.4, C | | | 101.9, C | | |
| | 5 | 157.2 ^l , C | | | 158.0 ^p , C | | |
| | 6 | 95.7 ^m , CH | 5.96 ⁿ , d (2.3) | 5.97 ^o , d (2.4) | 95.8 ^q , CH | 5.95 ^r , d (2.3) | 5.97 ^s , d (2.4) |
| | 7 | 158.3, C | | | 157.8 ^e , C | | |
| | 8 | 95.8 ^m , CH | 5.98 ⁿ , d (2.3) | 6.00 ^o , d (2.3) | 95.8 ^q , CH | 5.99 ^r , d (2.3) | 5.98 ^s , d (2.4) |
| | 8a | 157.4 ^l , C | | | 157.8 ^{e,m} , C | | |
| | 1' | 132.6, C | | | 132.5, C | | |
| | 2' | 114.9, CH | 6.89 ^a , d (1.7) | 6.89 ^c , d (1.8) | 114.8, CH | 6.90 ^g , d (1.6) | 6.90 ⁱ , d (1.8) |
| | 3' | 145.6, C | | | 145.6, C | | |
| | 4' | 145.3, C | | | 145.3, C | | |
| | 5' | 115.7, CH | 6.73, d (8.2) | 6.73 ^d , d (8.1) | 115.7, CH | 6.73 ^h , d (8.3) | 6.74 ^j , d (8.0) |
| 6' | 118.9, CH | 6.64–6.70 ^b | 6.70 ^d | 118.9, CH | 6.66–6.70 ^h | 6.67–6.72 ^j | |
| Middle unit | 2 | 76.7, CH | 5.26, bs | H ₂ O-signal | 76.8, CH | 5.31, bs | 5.29, bs |
| | 3 | 73.2, CH | 3.90, d (2.1) | 3.93, d (2.0) | 72.4, CH | 4.07, d (1.6) | 4.07, d (1.7) |
| | 4 | 37.1, CH | 4.68, bs | 4.69, m | 37.0, CH | 4.77, bs | 4.76, bs |
| | 4a | 102.0, C | | | 102.5, C | | |
| | 5 | 157.0, C | | | 157.0, C | | |
| | 6 | 96.6, CH | 5.88, s | 5.89, s | 96.6, CH | 5.87, s | 5.88, s |
| | 7 | 155.9, C | | | 156.8, C | | |
| | 8 | 106.8, C | | | 106.2, C | | |
| | 8a | 154.1, C | | | 154.9, C | | |
| | 1' | 132.6, C | | | 132.8, C | | |
| | 2' | 114.8, CH | 7.02, d (1.3) | 7.02, d (1.6) | 114.6, CH | 7.04, d (1.5) | 7.04, d (1.7) |
| | 3' | 145.8, C | | | 145.7, C | | |
| | 4' | 145.3, C | | | 145.1, C | | |
| | 5' | 115.7, CH | 6.64–6.70 ^b | 6.71 ^d , d (8.6) | 115.7, CH | 6.68 ^h , d (8.3) | 6.69, d (8.2) |
| 6' | 118.4, CH | 6.64–6.70 ^b | 6.69 ^d , d (6.9) | 118.5, CH | 6.78, dd (8.1, 1.7) | 6.79, dd (8.2, 1.9) | |

Table S2. Cont.

| | 5 (PC C1) | | | 6 (Epicatechin- β (4 \rightarrow 8)-epicatechin- β (4 \rightarrow 8)-catechin) | | | |
|------------------|-----------|-----------------------------|--|--|-----------------------------|--|--|
| | Pos. | δ_C type (-40 °C) | δ_H (J in Hz) (-40 °C) | δ_H (J in Hz) (-20 °C) | δ_C type (-40 °C) | δ_H (J in Hz) (-40 °C) | δ_H (J in Hz) (-20 °C) |
| Terminal unit | 2 | 79.4, CH | 4.99, bs | 4.99, bs | 81.3, CH | 5.06 ^f , d (4.6) | 5.02, d (4.7) |
| | 3 | 66.8, CH | 4.30, m | 4.31, m | 68.0, CH | 4.21, q (4.7) | 4.19, dd (10.2, 5.1) |
| | 4 | 29.9, CH ₂ | 2.80, d (16.1) 2.95, dd (16.6, 4.1) | 2.81, dd (16.9, 1.8) 2.95, dd (16.6, 4.1) | 25.9, CH ₂ | 2.50, dd (15.7, 2.8) 2.62, dd (16.4, 4.4) | 2.56 ^k , dd (16.6, 4.9) 2.62 ^k , dd (16.9, 5.2) |
| | 4a | 99.7, C | | | 99.8 | | |
| | 5 | 156.9, C | | | 155.7, C | | |
| | 6 | 97.0, CH | 5.93, s | 5.93, s | 96.8, CH | 5.89, s | 5.89, s |
| | 7 | 156.1, C | | | 156.4, C | | |
| | 8 | 107.5, C | | | 108.1, C | | |
| | 8a | 154.1, C | | | 153.6, C | | |
| | 1' | 132.0, C | | | 132.3, C | | |
| | 2' | 115.0, CH | 7.10, d (1.7) | 7.11, d (1.8) | 113.5, CH | 6.83, d (1.4) | 6.86, d (1.8) |
| | 3' | 146.0, C | | | 146.0, C | | |
| | 4' | 145.3, C | | | 145.6, C | | |
| | 5' | 115.6, CH | 6.74, d (8.2) | 6.75, d (8.2) | 115.9, CH | 6.71 ^h , d (8.3) | 6.72 ^j , d (8.0) |
| | 6' | 118.7, CH | 6.88 ^a , dd (8.0, 1.5) | 6.90 ^c , dd (8.2, 1.9) | 119.0, CH | 6.92 ^g , dd (8.5, 1.6) | 6.90 ⁱ , dd (8.1, 1.8) |

^{a-k} Signals with the same letter are overlapped; ^{l-s} Signals with the same letter are interchangeable.

Table S3. NMR data for compound 7.

| Pos. | 7 (Epicatechin- β (4 \rightarrow 8)-epicatechin- β (4 \rightarrow 8)-epicatechin- β (4 \rightarrow 8)-catechin) | | | |
|-------------------|---|-----------------------------------|-----------------------------------|-----------------------------|
| | δ_C type (-40 °C) | δ_H (J in Hz) (-40 °C) | δ_H (J in Hz) (-20 °C) | |
| Upper unit | 2 | 76.5, CH | 5.28, bs | H ₂ O-signal |
| | 3 | 73.2, CH | 4.08, d (1.6) | 4.10 ^g , d (2.1) |
| | 4 | 37.3, CH | 4.74, bs | 4.75, bs |
| | 4a | 102.3, C | | |
| | 5 | 157.9 ^{a,k} , C | | |
| | 6 | 95.7 ^l , CH | 5.96 ^m , d (2.1) | 5.98 ⁿ , d (2.3) |
| | 7 | 158.9, C | | |
| | 8 | 95.8 ^l , CH | 5.99 ^m , d (2.2) | 6.01 ⁿ , d (2.3) |
| | 8a | 157.9 ^{a,k} , C | | |
| | 1' | 132.6, C | | |
| | 2' | 114.7, CH | 7.11, d (1.0) | 7.10, d (1.6) |
| | 3' | 145.7 ^b , C | | |
| | 4' | 145.1, C | | |
| | 5' | 115.7, CH | 6.69–6.72 ^d | 6.70 ^h , d (8.1) |
| 6' | 118.4, CH | 6.75 ^d , m* | 6.77, dd (8.5, 1.7) | |
| Upper middle unit | 2 | 76.7, CH | 5.09 ^e , bs | 5.08, bs |
| | 3 | 73.6, CH | 3.97, d (1.6) | 3.99, d (1.8) |
| | 4 | 36.9, CH | 4.72, bs | 4.72, bs |
| | 4a | 102.1, C | | |
| | 5 | 157.3, C | | |
| | 6 | 96.8, CH | 5.92, s | 5.93, s |
| | 7 | 156.7, C | | |
| | 8 | 106.5, C | | |
| | 8a | 155.0, C | | |
| | 1' | 132.5, C | | |
| | 2' | 114.9, CH | 6.90, d (1.6) | 6.90 ⁱ , d (1.5) |
| | 3' | 145.8 ^c , C | | |
| | 4' | 145.3, C | | |
| | 5' | 115.7, CH | 6.74 ^d , m | 6.74 ^h , d (8.1) |
| 6' | 118.9, CH | 6.68 ^d , dd (8.1, 1.3) | 6.69 ^h , dd (8.5, 1.7) | |

Table S3. Cont.

| | Pos. | 7 (Epicatechin- β (4 \rightarrow 8)-epicatechin- β (4 \rightarrow 8)-epicatechin- β (4 \rightarrow 8)-catechin) | | |
|-------------------|-----------|---|--|--|
| | | δ_C type (-40 °C) | δ_H (J in Hz) (-40 °C) | δ_H (J in Hz) (-20 °C) |
| Lower middle unit | 2 | 76.8, CH | 5.37, bs | 5.34, bs |
| | 3 | 72.1, CH | 4.12, d (1.3) | 4.11 ^g , d (2.1) |
| | 4 | 37.1, C | 4.79, bs | 4.78, bs |
| | 4a | 102.7, C | | |
| | 5 | 157.7, C | | |
| | 6 | 96.8, CH | 5.93, s | 5.92, s |
| | 7 | 156.4, C | | |
| | 8 | 107.0, C | | |
| | 8a | 154.8, C | | |
| | 1' | 132.7, C | | |
| | 2' | 114.8, CH | 7.04, d (1.4) | 7.05, d (1.7) |
| | 3' | 145.8 ^c , C | | |
| | 4' | 145.2, C | | |
| | 5' | 115.7, CH | 6.70 ^d , m | 6.72 ^h , m |
| 6' | 118.6, CH | 6.82 ^f , m | 6.82, dd (8.3, 1.2) | |
| Terminal unit | 2 | 81.3, CH | 5.08 ^e , d (4.5) | 5.04, d (5.0) |
| | 3 | 68.0, CH | 4.22, m | 4.19, m |
| | 4 | 25.9, CH ₂ | 2.50, dd (16.5, 4.6) 2.62, dd (16.7, 4.6) | 2.56 ^j , dd (16.5, 4.6) 2.63 ^j , dd (16.7, 4.6) |
| | 4a | 99.8, C | | |
| | 5 | 155.7, C | | |
| | 6 | 96.5, CH | 5.89, s | 5.89, s |
| | 7 | 157.9 ^a , C | | |
| | 8 | 108.1, C | | |
| | 8a | 153.6, C | | |
| | 1' | 132.3, C | | |
| | 2' | 113.5, CH | 6.84 ^f , d (1.3) | 6.87, d (1.8) |
| | 3' | 146.1, C | | |
| | 4' | 145.7 ^b , C | | |
| | 5' | 115.7, CH | 6.71 ^d , m, | 6.72 ^h , m |
| 6' | 119.0, CH | 6.93, dd (8.5, 1.3) | 6.91 ⁱ , dd (8.4, 1.7) | |

^{a-j} Signals with the same letter are overlapped; ^{k-n} Signals with the same letter are interchangeable.

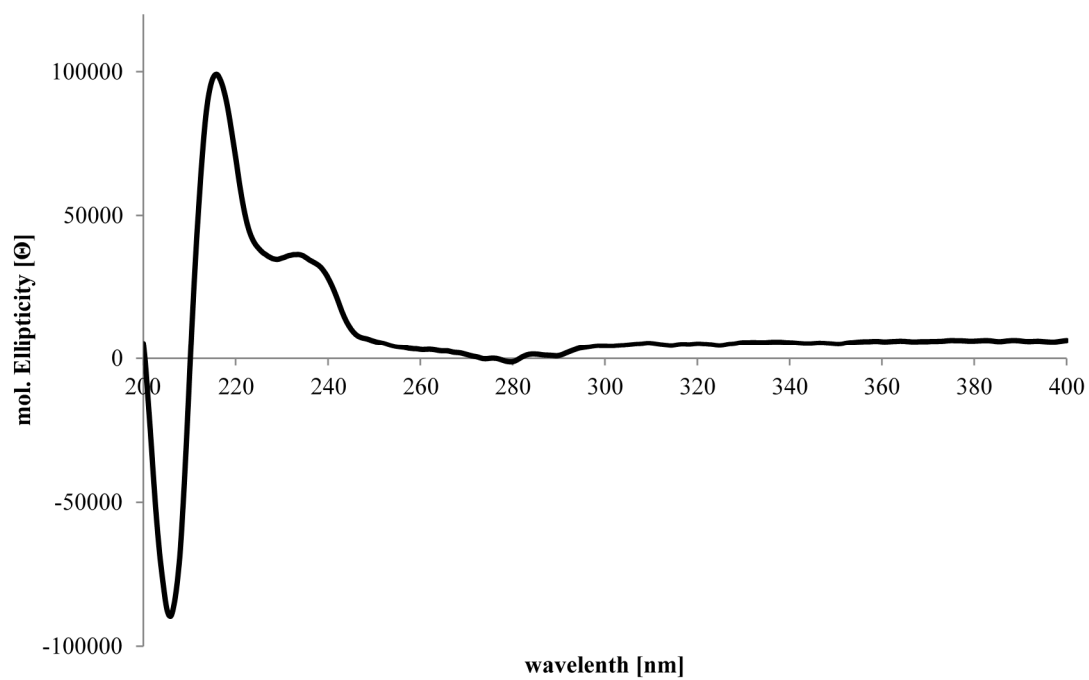


Figure S1. CD-spectrum of compound 1.

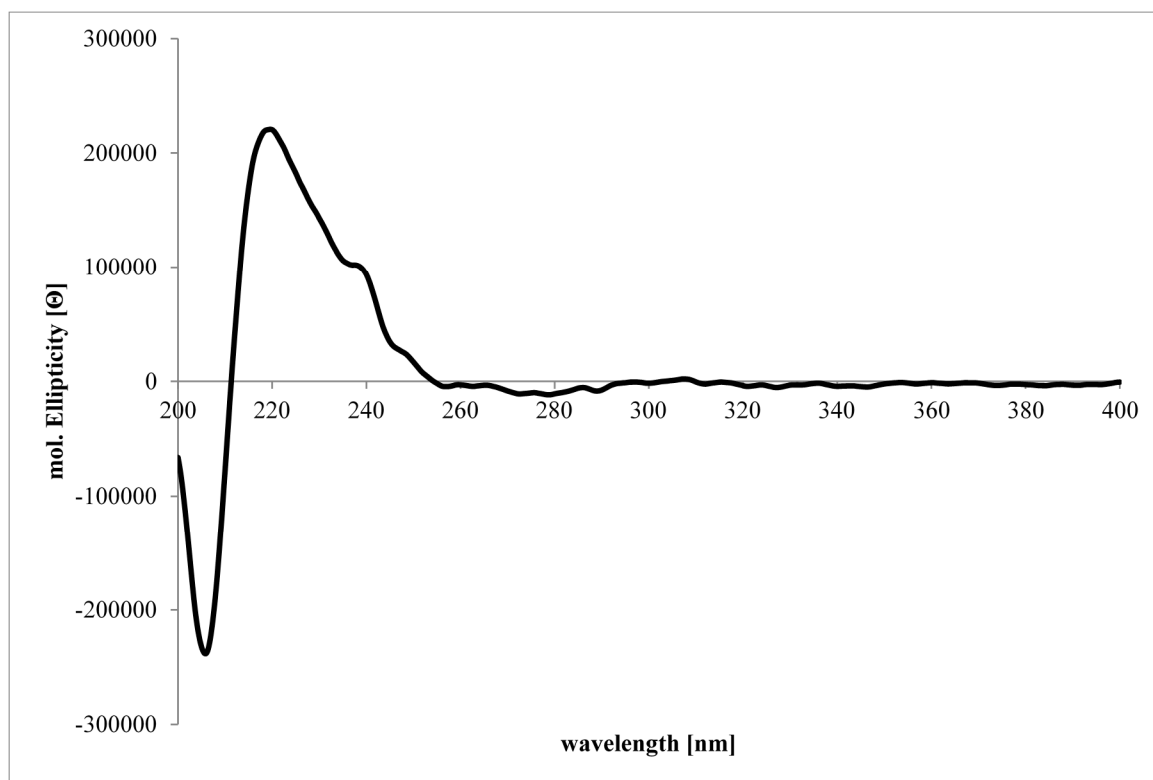


Figure S2. CD-spectrum of compound 7.

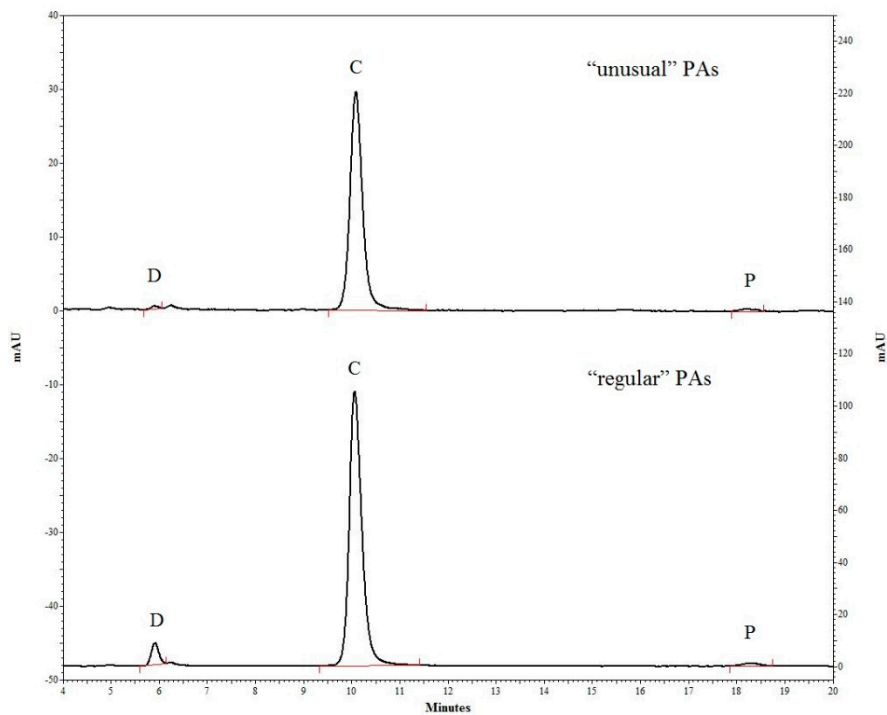


Figure S3. HPLC chromatograms after the cleavage reaction achieved by HCl/O₂. The left y-axis indicates the absorbance of the upper chromatogram (“unusual” PAs) and the right y-axis for the lower one (“regular” PAs) respectively. D = delphinidin, C = cyanidin, P = pelargonidin.

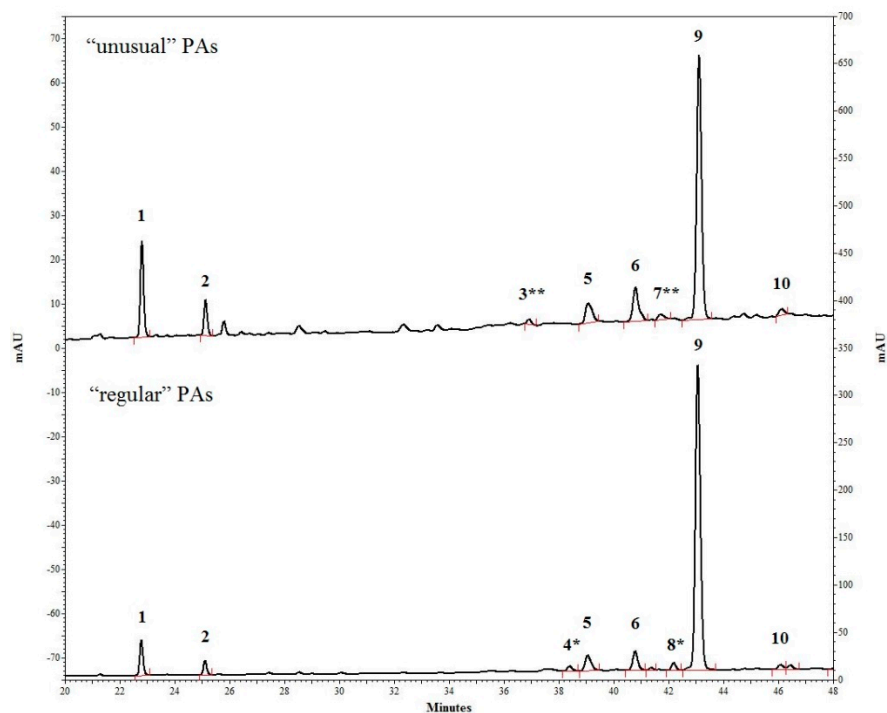


Figure S4. HPLC chromatograms after thiolysis. The left y-axis indicates the absorbance of the upper chromatogram (“unusual” PAs) and the right y-axis for the lower one (“regular” PAs), respectively. The peak numbers are explained in Table 2 of the main text.