

*Supporting Information*

**Total synthesis of cucurbitaxanthin A, cycloviolaxanthin and capsanthin 3,6-epoxide  
applying regioselective ring opening of tetrasubstituted epoxides**

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Synthesis and characterization data of compounds **15, 16, 18, 10a-f, 20c, 20d, 21c-d** and **22a-c**.

**(2E,4E)-5-[(1S,4S,6R)-4-tert-Butyldimethylsilyloxy-2,2,6-trimethyl-7-oxabicyclo[4.1.0]heptan-1-yl]-3-methylpenta-2,4-dienyl acetate 15**

A solution of the ester **13** (350 mg, 0.86 mmol) in dry ether (10 ml) was added dropwise to a stirred suspension of LiAlH<sub>4</sub> (33 mg, 0.87 mmol) in dry ether (10 ml) at 0 °C. After being stirred at 0 °C for 15 min, the excess of LiAlH<sub>4</sub> was decomposed by dropwise addition of water. The mixture was extracted with ether followed by standard work-up to provide the crude alcohol, which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 ml) and Py (0.35 ml, 4.3 mmol) and then acetic anhydride (0.24 ml, 2.5 mmol) were added. The mixture was stirred at room temp. for 3 h, poured into chilled water and extracted with ether. The extracts were washed with aq. 3% HCl, saturated aq. NaHCO<sub>3</sub>, and brine. Evaporation of the dried extracts gave a residue, which was purified by short CC (ether-hexane, 1:4) to give the acetate **15** (294 mg, 84%) as a colorless oil; [ $\alpha$ ]<sub>D</sub><sup>25</sup> -48.0 (*c* 1.00, MeOH);  $\nu_{\max}/\text{cm}^{-1}$  1732, 1627;  $\delta_{\text{H}}$ (300 MHz) 0.04 and 0.05 (each 3H, s), 0.88 (9H, s), 0.95, 1.12 and 1.16 (each 3H, s), 1.25 (1H, dd, *J* 13 and 10), 1.50 (1H, ddd, *J* 13, 3 and 1.5), 1.64 (1H, dd, *J* 14.5 and 8.5), 1.83 (3H, br s), 2.07 (3H, s), 2.24 (1H, ddd, *J* 14.5, 5.5 and 1.5), 3.85 (1H, m), 4.71 (2H, d, *J* 7), 5.60 (1H, br t, *J* 7), 5.92 and 6.23 (each 1H, d, *J* 16); *m/z* (EI) 408.2715 (M<sup>+</sup>, C<sub>23</sub>H<sub>40</sub>O<sub>4</sub>Si requires 408.2694).

**(3E)-4-[(1S,4S,6R)-4-tert-Butyldimethylsilyloxy-2,2,6-trimethyl-7-oxabicyclo[4.1.0]heptan-1-yl]but-3-en-2-one 16**

To a solution of the aldehyde **12**<sup>12</sup> (377 mg, 1.27 mmol) in toluene (15 ml) was added 1-triphenylphosphoranylidene-2-propanone (1.61 g, 5.06 mmol) and the mixture was refluxed for 17 h. After cooling, the mixture was filtered and the filtrate was evaporated. The residue was purified by short CC (ether-hexane, 1:9 to 15:85) to give the ketone **16** (385 mg, 90%) as a colorless oil; [ $\alpha$ ]<sub>D</sub><sup>22</sup> -73.1 (*c* 1.14, MeOH);  $\lambda_{\max}$ (EtOH)/nm 232;  $\nu_{\max}/\text{cm}^{-1}$  1693 and 1673 (split.), 1626;  $\delta_{\text{H}}$ (300 MHz) 0.04 and 0.05 (each 3H, s), 0.88 (9H, s), 0.95, 1.17 and 1.18 (each 3H, s), 1.27 (1H, dd, *J* 13 and 10), 1.51 (1H, ddd, *J* 13, 3.5 and 1.5), 1.67 (1H, dd, *J* 15 and 8), 2.25 (1H, ddd, *J* 15, 5 and 1.5), 2.28 (3H, s), 3.85 (1H, m), 6.27 and 7.03 (each 1H, d, *J* 15.5); *m/z* (EI) 338.2276 (M<sup>+</sup>, C<sub>19</sub>H<sub>34</sub>O<sub>3</sub>Si requires 338.2276).

**(2E,4E)-5-[(1S,4S,6R)-4-tert-Butyldimethylsilyloxy-2,2,6-trimethyl-7-oxabicyclo[4.1.0]heptan-1-yl]-3-methylpenta-2,4-dienitrile 18**

A solution of the phosphonate **17**<sup>13</sup> (1.31 g, 6.0 mmol) in dry THF (5 ml) was added dropwise to a stirred suspension of NaH (60% oil dispersion; 252 mg, 6.3 mmol) in dry THF (10 ml) at 0 °C. After being stirred at 0 °C for 15 min, a solution of the aldehyde **12** (1.25 g, 4.2 mmol) in dry THF (5 ml) was added. After being stirred at 0 °C for 30 min, the reaction was quenched by addition of saturated aq. NH<sub>4</sub>Cl. The mixture was extracted with ether followed by standard work-up to give a residue, which was purified by CC (ether-hexane, 1:4) to yield the epoxy dienonitrile **18** (1.21 g, 80%) and its 9Z isomer (226 mg, 15%) as a colorless oil, respectively.

**Compound 18.**  $[\alpha]_{\text{D}}^{22}$  -85.4 (*c* 0.82, MeOH);  $\lambda_{\text{max}}$ (EtOH)/nm 261;  $\nu_{\text{max}}$ /cm<sup>-1</sup> 2215, 1635, 1591;  $\delta_{\text{H}}$ (300 MHz) 0.05 (6H, s), 0.88 (9H, s), 0.94 (3H, s), 1.15 (6H, s), 1.28 (1H, dd, *J* 13 and 10), 1.51 (1H, ddd, *J* 13, 3.5 and 1.5), 1.66 (1H, dd, *J* 14.5 and 8), 2.17 (3H, d, *J* 1), 2.25 (1H, ddd, *J* 14.5, 5 and 1.5), 3.85 (1H, m), 5.23 (1H, d-like, *J* 1), 6.29 and 6.35 (each 1H, d, *J* 15.5); *m/z* (EI) 361.2435 (M<sup>+</sup>, C<sub>21</sub>H<sub>35</sub>NO<sub>2</sub>Si requires 361.2435).

**9Z Isomer of 18.**  $[\alpha]_{\text{D}}^{23}$  -25.1 (*c* 1.00, MeOH);  $\lambda_{\text{max}}$ (EtOH)/nm 261;  $\nu_{\text{max}}$ /cm<sup>-1</sup> 2216, 1636, 1589;  $\delta_{\text{H}}$ (300 MHz) 0.04 (6H, s), 0.87 (9H, s), 0.96, 1.14 and 1.16 (each 3H, s), 1.25 (1H, dd, *J* 13 and 10), 1.51 (1H, ddd, *J* 13, 3.5 and 1.5), 1.65 (1H, dd, *J* 14.5 and 8), 2.01 (3H, d, *J* 1), 2.25 (1H, ddd, *J* 14.5, 5 and 1.5), 3.85 (1H, m), 5.16 (1H, br s), 6.37 and 6.80 (each 1H, d, *J* 15.5); *m/z* (EI) 361.2432 (M<sup>+</sup>, C<sub>21</sub>H<sub>35</sub>NO<sub>2</sub>Si requires 361.2435).

### Desilylation of compounds **13**, **15**, **16** and **18**

To a solution of the silyl ether **13** (1.10 g, 2.7 mmol) in THF (20 ml) was added TBAF (1.0 M in THF; 5.4 ml, 5.4 mmol) and the mixture was stirred at 50 °C for 3.5 h. The reaction mixture was concentrated to give a residue, which was purified by short CC (acetone-hexane, 3:7) to afford the alcohol **10e** (780 mg, 98%). The compounds **10a** (89%), **10d** (84%) and **10f** (91%) were similarly prepared from the silyl ethers **16**, **15** and **18**, respectively.

**Compound 10a.** Colorless solid.  $[\alpha]_{\text{D}}^{23}$  -133.6 (*c* 1.13, MeOH);  $\lambda_{\text{max}}$ (EtOH)/nm 232;  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3608, 3473, 1694 and 1674 (split.), 1626;  $\delta_{\text{H}}$ (300 MHz) 0.98 (3H, s), 1.19 (6H, s), 1.27 (1H, dd, *J* 13 and 10), 1.63 (1H, ddd, *J* 13, 3.5 and 1.5), 1.66 (1H, dd, *J* 14.5 and 8.5), 2.28 (3H, s), 2.39 (1H, ddd, *J* 14.5, 5 and 1.5), 3.90 (1H, m), 6.29 and 7.03 (each 1H, d, *J* 15.5); *m/z* (EI) 224.1420 (M<sup>+</sup>, C<sub>13</sub>H<sub>20</sub>O<sub>3</sub> requires 224.1411).

**Compound 10d.** Colorless oil.  $[\alpha]_{\text{D}}^{23}$  -51.3 (*c* 0.92, MeOH);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3607, 3467, 1732, 1627;

$\delta_{\text{H}}$ (300 MHz) 0.97, 1.14 and 1.18 (each 3H, s), 1.24 (1H, dd,  $J$  13 and 10.5), 1.62 (1H, ddd,  $J$  13, 3.5 and 1.5), 1.62 (1H, dd,  $J$  14.5 and 8.5), 1.83 (3H, d,  $J$  1), 2.06 (3H, s), 2.38 (1H, ddd,  $J$  14.5, 5 and 1.5), 3.90 (1H, m), 4.71 (2H, d,  $J$  7), 5.60 (1H, br t,  $J$  7), 5.92 and 6.24 (each 1H, d,  $J$  16);  $m/z$  (EI) 294.1840 ( $\text{M}^+$ ,  $\text{C}_{17}\text{H}_{26}\text{O}_4$  requires 294.1830).

**Compound 10e.** Colorless solid.  $[\alpha]_{\text{D}}^{25} -64.2$  ( $c$  1.06, MeOH);  $\lambda_{\text{max}}$ (EtOH)/nm 264;  $\nu_{\text{max}}/\text{cm}^{-1}$  3609, 3483, 1704, 1613;  $\delta_{\text{H}}$ (300 MHz) 0.97, 1.16 and 1.18 (each 3H, s), 1.26 (1H, dd,  $J$  13 and 10.5), 1.28 (3H, t,  $J$  7), 1.63 (1H, ddd,  $J$  13, 3.5 and 1.5), 1.64 (1H, dd,  $J$  14 and 8.5), 2.29 (3H, d,  $J$  1), 2.38 (1H, ddd,  $J$  14, 5 and 1.5), 3.90 (1H, m), 4.17 (2H, q,  $J$  7), 5.80 (1H, q,  $J$  1), 6.26 and 6.32 (each 1H, d,  $J$  15.5);  $m/z$  (EI) 294.1827 ( $\text{M}^+$ ,  $\text{C}_{17}\text{H}_{26}\text{O}_4$  requires 294.1830).

**Compound 10f.** Colourless oil.  $[\alpha]_{\text{D}}^{22} -106.0$  ( $c$  0.97, MeOH);  $\lambda_{\text{max}}$ (EtOH)/nm 261;  $\nu_{\text{max}}/\text{cm}^{-1}$  3609, 3484, 2215, 1634, 1591;  $\delta_{\text{H}}$ (300 MHz) 0.96 (3H, s), 1.17 (6H, s), 1.26 (1H, dd,  $J$  13 and 10.5), 1.63 (1H, ddd,  $J$  13, 3.5 and 1.5), 1.64 (1H, dd,  $J$  14.5 and 8.5), 2.17 (3H, d,  $J$  1), 2.38 (1H, ddd,  $J$  14.5, 5 and 1.5), 3.90 (1H, m), 5.25 (1H, d-like,  $J$  1), 6.33 (2H, s);  $m/z$  (EI) 247.1551 ( $\text{M}^+$ ,  $\text{C}_{15}\text{H}_{21}\text{NO}_2$  requires 247.1571).

### **(2E,4E)-5-[(1S,4S,6R)-4-Hydroxy-2,2,6-trimethyl-7-oxabicyclo[4.1.0]heptan-1-yl]-3-methylpenta-2,4-dienal 10b**

HF•Py (1 ml) was added to a solution of the silyl ether **14** (350 mg, 0.96 mmol) in THF (10 ml) at 0 °C. After being stirred at 0 °C for 30 min, the reaction mixture was diluted with ether. The organic layer was washed successively with brine, saturated aq.  $\text{NaHCO}_3$  and then brine. Evaporation of the dried solution gave a residue, which was purified by short CC (acetone-hexane, 3:7) to afford the alcohol **10b** (180 mg, 75%) as a pale yellow oil. Spectral data were identical with those reported.<sup>11</sup>

### **Ring opening of 3-hydroxy 5,6-epoxides 10a–f (Table 1)**

**Treatment with  $\text{SnCl}_4$ .** Each epoxide (*ca.* 0.1 M in dry  $\text{CH}_2\text{Cl}_2$ ) was treated with  $\text{SnCl}_4$  (1M in  $\text{CH}_2\text{Cl}_2$ ) under the conditions shown in Table 1. The mixture was then poured into saturated aq.  $\text{NaHCO}_3$  and extracted with ether. The extracts were followed by standard work-up to give a residue, which was purified by short CC (acetone-hexane, 1:9~3:7).

**Treatment with aminium salt 19.** Each epoxide (*ca.* 0.1 M in dry  $\text{CH}_2\text{Cl}_2$ ) was treated with tris(4-bromophenyl)aminium hexachloroantimonate **19** under the conditions shown in Table 1. The

mixture was then concentrated to give a residue, which was purified by short CC (acetone-hexane, 1:9~3:7).

**Compound 20c.** Colorless oil.  $^1\text{H}$  NMR data were identical with those reported.  $^{16}\nu_{\text{max}}/\text{cm}^{-1}$  3604, 3468, 1726;  $\delta_{\text{H}}(300\text{ MHz})$  0.87, 1.19 and 1.40 (each 3H, s), 1.33 (3H, d,  $J$  6.5), 1.59 (1H, d,  $J$  11.5), 1.65 (1H, d,  $J$  12.5), 1.81 (1H, ddd,  $J$  11.5, 6 and 2.5), 2.02 (1H, ddd,  $J$  12.5, 6 and 2.5), 2.04 (3H, s), 4.36 (1H, t,  $J$  6), 5.39 (1H, qd,  $J$  6.5 and 5), 5.69 (1H, dd,  $J$  16 and 5), 5.76 (1H, d,  $J$  16);  $m/z$  (CI) 269.1749 ( $\text{MH}^+$ ,  $\text{C}_{15}\text{H}_{25}\text{O}_4$  requires 269.1751).

**Compound 20d.** Pale yellow oil.  $\nu_{\text{max}}/\text{cm}^{-1}$  3603, 3476, 1731;  $\delta_{\text{H}}(300\text{ MHz})$  0.87, 1.20 and 1.43 (each 3H, s), 1.60 (1H, d,  $J$  11.5), 1.67 (1H, d,  $J$  12.5), 1.83 (1H, ddd,  $J$  11.5, 6 and 2.5), 2.05 (1H, ddd,  $J$  12.5, 6 and 2.5), 2.07 (3H, s), 4.39 (1H, t,  $J$  6), 4.72 (2H, d,  $J$  7), 5.60 (1H, br t,  $J$  7), 5.77 and 6.32 (each 1H, d,  $J$  16);  $m/z$  (EI) 294.1825 ( $\text{M}^+$ ,  $\text{C}_{17}\text{H}_{26}\text{O}_4$  requires 294.1830).

**Compound 21c (~1:1 mixture of 5,8-*cis* and 5,8-*trans* isomers).** Colorless oil.  $\nu_{\text{max}}/\text{cm}^{-1}$  3609, 3468, 1728;  $\delta_{\text{H}}(300\text{ MHz})$  1.16 and 1.23 (each 3/2H, d,  $J$  6.5), 1.18 and 1.32 (each 3H, s), 1.45 (1H, m), 1.60 and 1.65 (each 3/2H, s), 1.72-1.93 (2H, m), 2.05 and 2.07 (each 3/2H, s), 2.12 (1H, m), 4.21 (1H, m), 4.61 (1/2H, dd,  $J$  5.5 and 2), 4.84 (1/2H, dd,  $J$  3.5 and 1), 4.91 (1H, m), 5.25 (1/2H, d,  $J$  2), 5.27 (1/2H, d,  $J$  1);  $m/z$  (CI) 269.1752 ( $\text{MH}^+$ ,  $\text{C}_{15}\text{H}_{25}\text{O}_4$  requires 269.1751).

**Compound 21d (~1:10 mixture of 5,8-*cis* and 5,8-*trans* isomers).** Pale yellow oil.  $\nu_{\text{max}}/\text{cm}^{-1}$  3608, 3448, 1731;  $\delta_{\text{H}}(300\text{ MHz})$  1.18 and 1.33 (each 3H, s), 1.50 (1H, dd,  $J$  14.5 and 3.5), 1.61 (6H, s), 1.76 (1H, ddd,  $J$  14.5, 4.5 and 1.5), 1.95 (1H, dd,  $J$  14 and 4.5), 2.05 (3H, s), 2.12 (1H, ddd,  $J$  14, 4 and 1.5), 4.24 (1H, m), 4.60 and 4.66 (each 1H, dd,  $J$  12.5 and 7), 5.01 (1/11H, br s), 5.11 (10/11H, br s), 5.25 (10/11H, d,  $J$  1), 5.30 (1/11H, d,  $J$  2), 5.64 (1H, br t,  $J$  7);  $m/z$  (EI) 294.1839 ( $\text{M}^+$ ,  $\text{C}_{17}\text{H}_{26}\text{O}_4$  requires 294.1830).

**Compound 22a.** Pale yellow oil.  $\nu_{\text{max}}/\text{cm}^{-1}$  3611, 3470, 1702 and 1677 (split.), 1614;  $\delta_{\text{H}}(300\text{ MHz})$  0.84, 1.21 and 1.37 (each 3H, s), 1.52 (1H, dd,  $J$  14.5 and 3.5), 1.73 (1H, dd,  $J$  14 and 4.5), 1.98 (1H, dd,  $J$  14 and 7.5), 2.36 (3H, s), 2.88 (1H, dd,  $J$  14.5 and 8.5), 4.50 (1H, m), 6.91 and 7.21 (each 1H, d,  $J$  15.5);  $m/z$  (EI) 224.1427 ( $\text{M}^+$ ,  $\text{C}_{13}\text{H}_{20}\text{O}_3$  requires 224.1411).

**Compound 22b.** Spectral data were identical with those previously reported.<sup>1</sup>

**Compound 22c.** Colorless oil.  $\nu_{\text{max}}/\text{cm}^{-1}$  3611, 3468, 1732, 1686, 1629;  $\delta_{\text{H}}(300\text{ MHz})$  0.81, 1.17 and 1.33 (each 3H, s), 1.36 (3H, d,  $J$  6.5), 1.47 (1H, dd,  $J$  14.5 and 3.5), 1.70 (1H, dd,  $J$  13.5 and 4.5), 1.97 (1H, dd,  $J$  13.5 and 7.5), 2.09 (3H, s), 2.89 (1H, dd,  $J$  14.5 and 8.5), 4.48 (1H, m), 5.48 (1H, m),

6.51 (1H, dd, *J* 15.5 and 1.5), 6.73 (1H, dd, *J* 15.5 and 5); *m/z* (CI) 269.1727 (MH<sup>+</sup>, C<sub>15</sub>H<sub>25</sub>O<sub>4</sub> requires 269.1751).