Synthesis of analogues of citranaxanthin and their activity in free radical scavenging

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Citranaxanthin and its analogues were synthesised *via* a C_5 unit elongation to substituted conjugated polyenes. Their free radical scavenging activity was measured by 1,1-diphenyl-2-picrylhydrazinyl spectrophotometric methods. Results indicated that the new compounds exhibited antioxidant activities. Three new analogues had stronger antioxidant activity than citranaxanthin.

Keywords: citranaxanthin, antioxidant activity, β-apo-8'-carotenal

Citranaxanthin (CTX) (**1**) (Fig. 1) is the first known naturally occurring carotenoid with a methyl ketone grouping in the side chain.[1] It has free-radical scavenging ability[2–4] and can be used in pharmaceuticals, pigments, feed additives and aquaculture.[5–6] Related carotenoids play an important role in the prevention of certain human diseases such as cardiovascular disease and cancer.[7–9] Higher nutritional uptake of CTX may increase macular pigment density and thereby lower the risk of age-related macular degeneration (AMD). AMD is the main cause of loss of vision in western countries.[10–11]

In 1996, some CTX analogues were synthesised and used in egg colouring. They have a low deposition efficiency in yolks.[12] In the present work, a series of new CTX analogues were designed and synthesised by condensation of methyl ketones with β-apo-8'-carotenal (**12**) or β-apo-12'-carotenal (**11**). The structures of the new compounds were characterised by NMR, HRMS, IR and UV-Vis. The free radical scavenging activity of the samples was measured using a WD-2102A automatic enzyme instrument with 1,1-diphenyl-2-picrylhydrazinyl (DPPH) as the organic free radical.

Results and discussion

Synthesis of β*-apo-8'-carotenal (***12***) and* β*-apo-12'-carotenal* (**11**)

Isoprene was used as a starting material (Scheme 1).

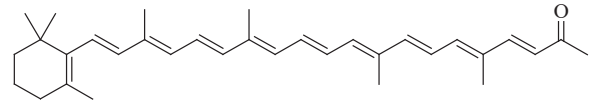
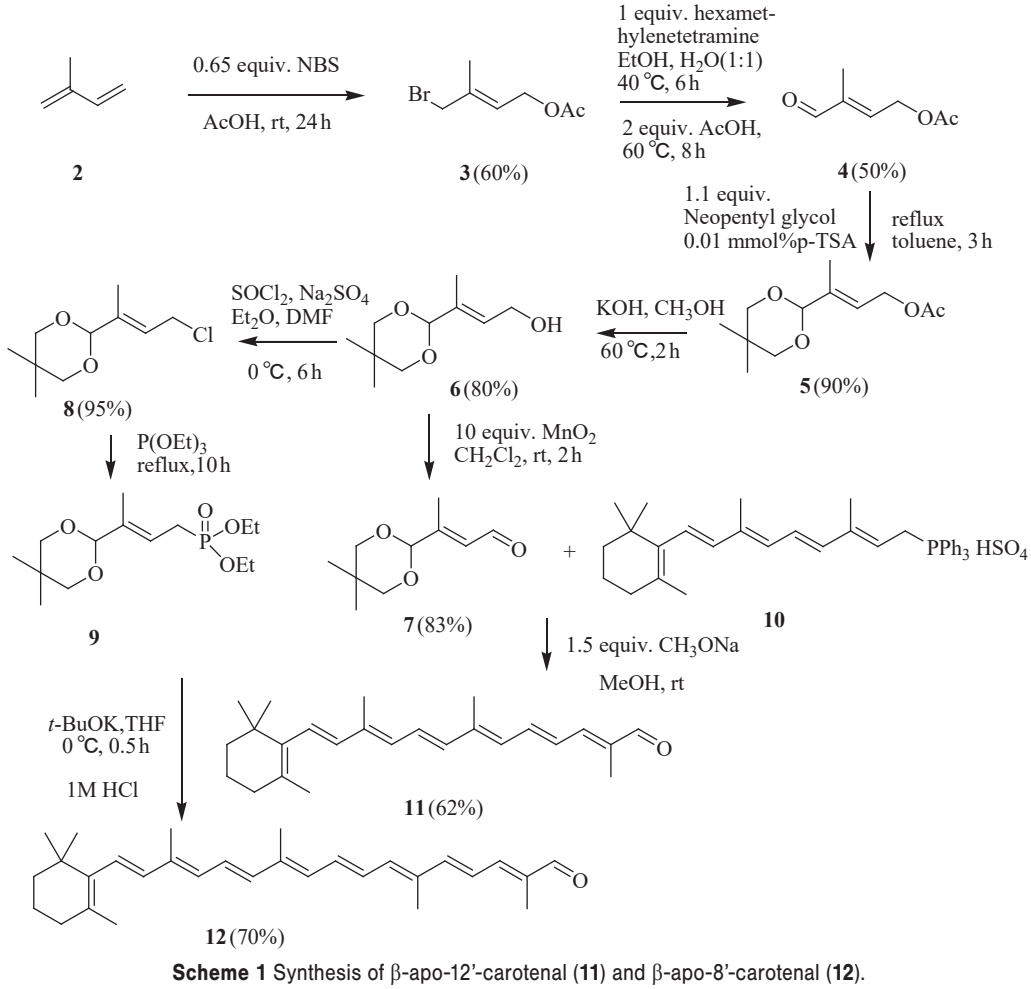


Fig. 1 Structure of citranaxanthin (CTX) (**1**).



Scheme 1 Synthesis of β-apo-12'-carotenal (**11**) and β-apo-8'-carotenal (**12**).

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Compound **3** was synthesised from the reaction of **2** with *N*-bromosuccinimide (NBS) in 60% yield.[13] Ethanol was used as the solvent in the synthesis of **4** from **3**, to assist isolation.[14] Compounds **5**, **6** and **8** were successfully synthesised in 90%, 80% and 95% yields respectively.[15] The above products were purified by distillation under reduced pressure. Compound **6** was then oxidised with manganese dioxide to form the aldehyde **7** in 83% yield.[16]

The Wittig salt **10** was prepared by the equimolar addition of triphenylphosphonium sulfate to a stirred solution of vitamin A acetate (provided by Guangzhou Juyuan Bio Chem Co. Ltd) in dry methanol.[17] β-Apo-12'-carotenal (**11**) was prepared from **7** with the Wittig salt **10** in 62% yield. Only **11** was obtained.[18] Compound **8** was refluxed with triethyl phosphite for 10 h to give **9**. The phosphate reacted with potassium *tert*-butoxide and β-apo-12'-carotenal (**11**) to give β-apo-8'-carotenal (**12**) in 70% yield.

Synthesis of the analogues of CTX

The target compounds **13a–c** and **14a–c** were synthesised by reaction of β-apo-8'-carotenal (**12**) or β-apo-12'-carotenal (**11**) with methyl ketones and KOH at room temperature in high yields. The dark red crystals of the products were purified by silica column chromatography (Scheme 2).[19]

All the new compounds were characterised by NMR, HRMS, IR and UV-Vis. ^{1}H NMR showed the corresponding olefins with a chemical shift of 6 to 8 ppm. ^{13}C NMR showed the corresponding number of carbons and the peaks of carbonyl group carbon atoms (≈190 ppm) were found. The separation of *cis–trans* isomers was not possible by column chromatography because of similar retention times between them in different solvents.[20] The target compounds were unstable at high temperature.[21]

Determination of DPPH radical scavenging activity

The free radical scavenging activity of samples on 1,1-diphenyl-2-picrylhydrazinyl (DPPH) was obtained using the method of Sharma and Bhat (2009) with slight modifications.[22] Briefly, a DPPH working solution (200 μM) was freshly prepared in methanol (spectroscopic grade) by stirring for at least 15–20 min and was used within 3 h of preparation. A solution of DPPH (200 μL, 0.1 mM) was added to 100 μL of a 10 mg L^{-1} sample. The mixture was shaken and left to stand at room temperature in the dark. After 30 min, the absorbance of the mixture was measured at 517 nm. A solution of 100 μL test sample and 200 μL ethanol was used for zero setting.[23] Distilled water (100 μL) added to DPPH (200 μL, 0.1 mM) without addition of the test sample was used as a blank control reaction. A lower absorbance of the reaction mixture indicated greater free radical scavenging activity. The scavenging activity on DPPH radical (SADPPH) is defined as:

$$SADPPH = (1 - A_s/A_c) \times 100\%$$

where A_c is the absorbance of the blank control reaction and A_s is the absorbance in the presence of samples.

All synthetic new compounds and the known carotenoids showed DPPH radical scavenging effects (Fig. 2). The DPPH radical scavenging effects of the carotenoids decreased in the order of **14a** > **14b** > β-carotene > **12** > **14c** > CTX > **13c** > **13b** > **13a** and were 54.20%, 53.17%, 41.30%, 39.02%, 36.96%, 36.88%, 25.65%, 21.98% and 21.75% in 100 μL of solution. Compounds **14a** and **14b** had stronger antioxidant activity than citranaxanthin, β-carotene and compound **12**.

Conclusion

A series of new analogues of citranaxanthin was designed and synthesised by condensation of methyl ketones with **11** or **12** and their structures were confirmed. The free radical scavenging activity test showed that among 6 target compounds, **14a** and **14b** had stronger antioxidant activity than β-carotene and **12** and **14c** had stronger antioxidant activity than CTX. Among

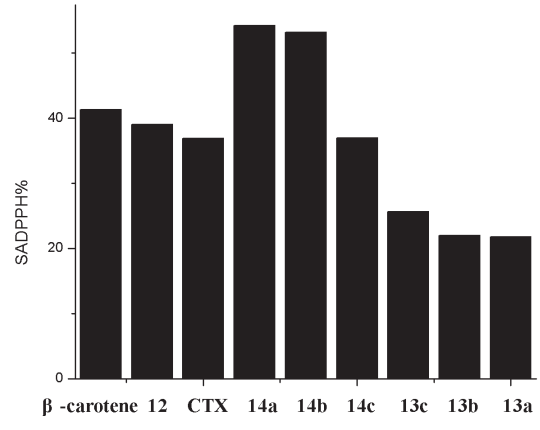
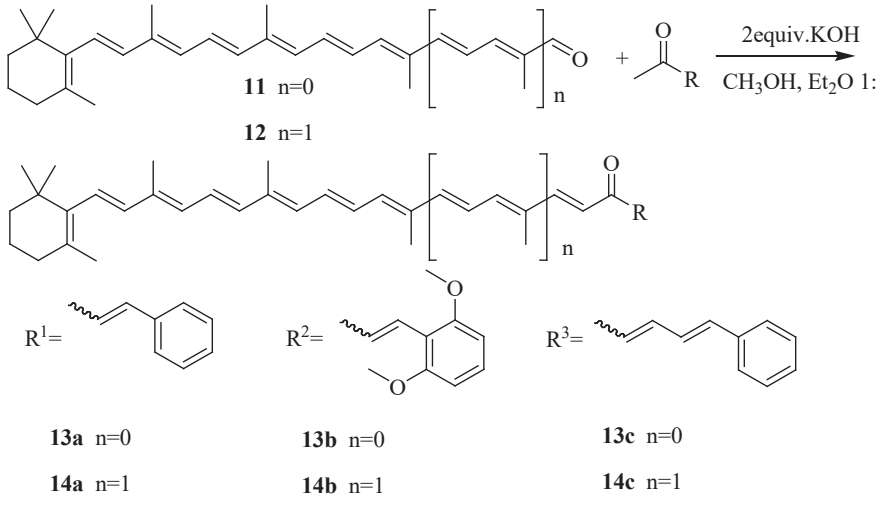


Fig. 2 The DPPH radical scavenging activity of the target compounds.



Scheme 2 Synthesis of the analogues of CTX.

the synthesised target compounds, **14a** had the best antioxidant activity. The target compounds with long chains have a better ability to eliminate free radicals.

Experimental

Reagents and starting materials obtained from commercial suppliers were used without further purification unless otherwise stated. The IR spectra were recorded on a PerkinElemer 16PC-FT spectrometer. NMR spectra were recorded on a Varian Unity Inova-400 spectrometer (Varian Inc., Palo Alto, CA, USA) with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) were obtained with a LCMS-IT-TOF spectrometer (Shimadzu, Japan) using electrospray ionisation (ESI). UV-Vis spectra were obtained on a UV3600 (Shimadzu, Japan) instrument. Flash chromatography was performed on > 300 mesh silica gel. Melting points were determined using a XRC-1 melting point apparatus (Sichuan University Instrument Inc., Chengdu, China) and were uncorrected.

Preparation of intermediates of **3**–**10**

The intermediates **3**–**9** were prepared from isoprene according to the literature. Compound **10** was also prepared according to the literature (see Results and discussion section).

2,7,11-Trimethyl-13-(2,6,6-trimethylcyclohex-1-enyl)trideca-2,4,6,8,10,12-hexaenal (**11**)

Sodium methoxide (0.81 g, 15 mmol) was added to a solution of **10** (6.28 g, 10 mmol) in dry methanol (30 mL) at 0 °C and the mixture was stirred about for 0.5 h. A solution of **7** (0.92 g, 5 mmol) in dry methanol (5 mL) was added and the mixture was stirred for 6 h. A solution of 1 M HCl (5 mL) was added to the mixture obtained above and this was stirred at room temperature for 3 h. The reaction mixture was diluted with water (25 mL) and extracted with Et_2O (3 × 25 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuum to give the C_{25}-aldehyde **11** (1.08 g, 62%). This was purified through silica column chromatography (5% ethyl acetate in petroleum ether) to give: m.p. 86–89 °C; IR (KBr): 2927, 1662 (C=O), 1607 (C=C), 1545, 1442, 1382, 1184 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.45 (d, *J* = 4.5 Hz, 1H), 7.08–6.92 (m, 2H), 6.79 (dd, *J* = 14.6 Hz, 1H), 6.67 (dd, *J* = 14.6, 11.8 Hz, 1H), 6.40–6.33 (m, 1H), 6.32–6.26 (m, 1H), 6.26–6.20 (m, 1H), 6.15 (td, *J* = 11.1, 4.6 Hz, 2H), 2.03 (m, 2H, CH_2), 1.99 (s, 6H, CH_3), 1.87 (s, 3H, CH_3), 1.71 (s, 3H), 1.61 (m, 2H, CH_2), 1.48–1.44 (m, 2H, CH_2), 1.02 (s, 6H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.59, 149.21, 149.13, 141.93, 138.09, 137.91, 137.61, 136.87, 136.42, 130.92, 130.50, 129.95, 127.96, 127.84, 127.37, 39.74, 34.40, 33.26, 29.10, 21.91, 19.36, 13.20, 12.99, 9.73; UV (ethanol) max: 426 nm; HRMS calcd for $C_{25}H_{34}ONa$: $[M + Na]^+$: 373.2507; found: 373.2509.

2,6,11,15-Tetramethyl-17-(2,6,6-trimethylcyclohex-1-enyl)heptadeca-2,4,6,8,10,12,14,16-octaenal (**12**)

The phosphate **9** (0.50 g, 1.63 mmol) was added to a solution of *t*-BuOK (0.19 g, 1.70 mmol) in dry THF (15 mL). The mixture was stirred at room temperature for 30 min. Then a solution of **11** (0.35 g, 1 mmol) in dry THF (15 mL) was added and the mixture was stirred for 18 h in the dark at room temperature in a nitrogen atmosphere. A solution of 1 M HCl (20 mL) was added to the solution obtained above and the mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with water (30 mL) and extracted with Et_2O (3 × 25 mL). The organic layer was dried with Na_2SO_4 and concentrated in vacuum. The residue was purified by silica column chromatography (2.5% ethyl acetate in petroleum ether) to give: m.p. 126–128 °C; IR (KBr): 2922, 1667 (C=O), 1609 (C=C), 1514, 1401, 1380, 1357, 1182 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.45 (s, 1H), 6.95 (dd, *J* = 10.7, 1.0 Hz, 1H), 6.81–6.57 (m, 5H), 6.45 (d, *J* = 11.6 Hz, 1H), 6.36 (d, *J* = 14.9 Hz, 1H), 6.27 (d, *J* = 11.7 Hz, 1H), 6.19–6.08 (m, 3H), 2.02 (m, 2H, CH_2), 2.00 (s, 6H, 2 × CH_3), 1.98 (s, 3H, CH_3), 1.90 (s, 3H), 1.72 (s, 3H), 1.65–1.57 (m, 2H, CH_2), 1.49–1.44 (m, 2H, CH_2), 1.03 (s, 6H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.74, 149.54, 146.13, 138.80, 138.00, 137.78, 137.76, 137.06, 136.98, 136.81, 135.29, 133.18, 132.03, 130.79, 129.76, 129.27, 127.36, 126.35, 122.78, 39.76, 34.42, 33.27, 29.12, 21.93, 19.39, 13.09, 12.96, 12.86, 9.81; UV (ethanol) max: 464 nm; HRMS calcd for $C_{30}H_{40}ONa$: $[M + Na]^+$: 439.2977; found: 439.2973.

Synthesis of the target compounds **13a**–**c**, **14a**–**c** *and citranaxanthin* (**1**)*; general procedure*

β-Apo-8'-carotenal (**12**) (1 mmol) or β-apo-12'-carotenal (**11**) (1 mmol) was added to a mixture of the methyl ketone (2 mmol) and KOH (2 mmol) in 20 mL of diethyl ether/methanol (1:1) at 0 °C. Under ultrasound, the mixture was stirred for 3 min. Then the mixture was stirred for 18 h in the dark at room temperature in a nitrogen atmosphere. Acetic acid (5 mL) was added to the solution obtained above and the mixture was stirred at room temperature for 0.5 h. The resulting mixture was diluted with water (30 mL) and extracted with Et_2O (3 × 25 mL). The organic layer was washed three times with saturated sodium chloride and dried with Na_2SO_4 and concentrated in vacuum. The residue was purified by silica column chromatography (5% ethyl acetate in petroleum ether) to give the target compounds in 75–85% yield.

5,9,14,18-Tetramethyl-20-(2,6,6-trimethylcyclohex-1-enyl)icosa-3,5,7,9,11,13,15,17,19-nonaen-2-one (**1**): Yield 83%; m.p.: 110–118 °C; IR (KBr): 2918, 1657 (C=O), 1588 (C=C), 1513, 1442, 1360, 1255, 1187 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 15.8 Hz, 1H), 6.75–6.49 (m, 6H), 6.34 (dd, *J* = 14.0, 9.8 Hz, 2H), 6.19 (m, 5H), 2.32 (s, 3H, CH_3), 2.02 (m, 2H, CH_2), 1.98 (s, 6H, 2 × CH_3), 1.95 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.51–1.42 (m, 2H, CH_2), 1.23–1.31 (m, 2H, CH_2), 1.05 (s, 6H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.61, 148.08, 142.44, 140.69, 138.04, 137.95, 137.83, 137.14, 136.72, 135.89, 135.61, 133.57, 132.26, 131.98, 130.87, 129.65, 127.16, 125.91, 125.60, 124.05, 39.81, 34.43, 33.28, 29.13, 27.61, 21.92, 19.41, 13.04, 12.94, 12.88, 12.82; UV (ethanol) max: 472 nm; HRMS calcd for $C_{33}H_{44}ONa$: $[M + Na]^+$: 479.3290; found: 479.3290.

6,11,15-Trimethyl-17-(2,6,6-trimethylcyclohex-1-enyl)-1-phenylheptadeca-1,4,6,8,10,12,14,16-octaen-3-one (**13a**): Yield 80%; m.p. 36–48 °C; IR (KBr): 2925, 1666 (C=O), 1609 (C=C), 1449, 1360, 1257, 1182, 1102 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71–7.65 (m, 1H), 7.59 (dt, *J* = 5.2, 3.2 Hz, 2H), 7.47 (d, *J* = 15.4 Hz, 1H), 7.42–7.36 (m, 3H), 7.03 (d, *J* = 15.9 Hz, 1H), 6.87–6.79 (m, 1H), 6.74 (dd, *J* = 14.9, 11.5 Hz, 1H), 6.63 (dd, *J* = 7.9, 5.3 Hz, 2H), 6.54–6.48 (m, 1H), 6.36 (d, *J* = 14.9 Hz, 1H), 6.30–6.24 (m, 1H), 6.21–6.11 (m, 3H), 2.04 (m, 2H, CH_2), 2.02 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 1.61 (m, 2H, CH_2), 1.45 (m, 2H, CH_2), 1.03 (s, 6H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 188.89, 147.86, 142.51, 141.12, 139.66, 137.99, 137.75, 137.31, 136.89, 135.16, 134.55, 134.27, 131.83, 130.74, 130.37, 129.78, 129.03, 129.01, 128.43, 127.49, 126.74, 125.99, 124.30, 39.76, 34.41, 33.26, 29.11, 21.92, 19.38, 13.13, 12.96, 12.84; UV (ethanol) max: 327, 472 nm; HRMS calcd for $C_{35}H_{42}ONa$: $[M + Na]^+$: 501.3133; found: 501.3139.

1-(2,6-Dimethoxyphenyl)-6,11,15-trimethyl-17-(2,6,6-trimethylcyclohex-1-enyl)heptadeca-1,4,6,8,10,12,14,16-octaen-3-one (**13b**): Yield 78%; m.p. 90–95 °C; IR (KBr): 2923, 1598 (C=O), 1637 (C=C), 1473, 1324, 1225, 1181, 1107 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 16.2 Hz, 1H), 7.45 (dd, *J* = 15.8, 11.8 Hz, 2H), 7.31–7.27 (m, 1H), 6.85–6.52 (m, 7H), 6.36 (d, *J* = 14.9 Hz, 1H), 6.28 (d, *J* = 11.7 Hz, 1H), 6.25–6.09 (m, 3H), 3.90 (s, 6H, 2 × OCH_3), 2.04 (m, 2H, CH_2), 2.01 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 1.64–1.60 (m, 2H, CH_2), 1.49–1.44 (m, 2H, CH_2), 1.04 (s, 6H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.60, 160.27, 146.75, 139.08, 137.88, 137.67, 137.01, 136.86, 134.52, 133.81, 133.66, 131.82, 131.25, 130.66, 129.63, 129.08, 128.99, 127.25, 126.37, 124.96, 112.88, 103.72, 55.85, 39.64, 34.30, 33.15, 29.00, 21.81, 19.27, 13.00, 12.85, 12.81; UV (ethanol) max: 322, 474 nm; HRMS calcd for $C_{37}H_{46}O_3Na$: $[M + Na]^+$: 561.3345; found: 561.3341.

8,13,17-Trimethyl-19-(2,6,6-trimethylcyclohex-1-enyl)-1-phenylnonadeca-1,3,6,8,10,12,14,16,18-nonaen-5-one (**13c**): Yield in 75%. m.p. 32–36 °C; IR (KBr): 2920, 1652 (C=O), 1616 (C=C), 1446, 1360, 1253 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 3.5, 1.7 Hz, 3H), 7.35–7.29 (m, 4H), 6.92 (ddt, *J* = 19.4, 14.0, 4.5 Hz, 4H),

6.66–6.54 (m, 3H), 6.36 (d, *J* = 14.9 Hz, 1H), 6.31–6.22 (m, 2H), 6.21–6.11 (m, 3H), 2.04 (m, 2H, CH_2), 2.02 (s, 3H, CH_3), 1.99 (s, 6H, 2 × CH_3), 1.72 (s, 3H, CH_3), 1.64–1.58 (m, 2H, CH_2), 1.50–1.43 (m, 2H, CH_2), 1.03 (s, 6H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 188.85, 147.43, 143.09, 142.55, 141.51, 141.13, 140.85, 139.49, 137.88, 137.65, 137.18, 136.80, 136.25, 136.15, 134.35, 134.22, 131.73, 130.65, 129.67, 129.55, 129.10, 129.05, 127.02, 124.20, 39.65, 34.30, 33.16, 29.74, 29.02, 21.82, 19.28, 19.18, 13.03, 12.86, 12.73; UV (ethanol) max: 324, 477 nm; HRMS calcd for $C_{37}H_{45}O$: $[M + H]^+$: 505.3470; found: 505.3461.

6,10,15,19-Tetramethyl-21-(2,6,6-trimethylcyclohex-1-enyl)-1-phenylhenicosa-1,4,6,8,10,12,14,16,18,20-decaen-3-one (**14a**): Yield 85%. m.p. 86–96 °C; IR (KBr): 2914, 1658 (C=O), 1587 (C=C), 1442, 1360, 1256, 1186 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.33 (m, 7H), 6.97 (dd, *J* = 9.6, 6.9 Hz, 2H), 6.74–6.55 (m, 6H), 6.45 (d, *J* = 15.4 Hz, 1H), 6.37 (dd, *J* = 12.8, 6.8 Hz, 2H), 6.29–6.23 (m, 1H), 6.15 (dd, *J* = 14.1, 9.8 Hz, 2H), 2.02 (m, 2H), 2.01 (s, 3H, CH_3), 1.99 (s, 6H, 2 × CH_3), 1.98 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 1.63–1.60 (m, 2H, CH_2), 1.50–1.44 (m, 2H, CH_2), 1.03 (s, 6H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 189.04, 148.17, 142.68, 142.57, 141.49, 137.99, 137.96, 137.79, 137.12, 136.67, 135.92, 135.80, 135.11, 133.92, 132.28, 132.05, 130.87, 130.36, 129.65, 129.61, 129.00, 128.42, 127.42, 127.11, 126.93, 125.89, 124.06, 71.69, 39.76, 34.38, 33.23, 29.80, 29.09, 21.88, 21.44, 19.37, 13.00, 12.89, 12.86, 12.83; UV (ethanol) max: 316, 498 nm; HRMS calcd for $C_{40}H_{49}O$: $[M + H]^+$: 545.3783; found: 545.3776.

1-(2,6-Dimethoxyphenyl)-6,10,15,19-tetramethyl-21-(2,6,6-trimethylcyclohex-1-enyl)henicosa-1,4,6,8,10,12,14,16,18,20-decaen-3-one (**14b**): Yield 80%; m.p. 110–124 °C; IR (KBr): 2926, 1595 (C=O), 1588 (C=C), 1474, 1383, 1257, 1180, 1108 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 16.2 Hz, 1H), 7.49 (dd, *J* = 21.5, 5.3 Hz, 2H), 7.28 (t, *J* = 6.3 Hz, 1H), 6.69 (dd, *J* = 18.4, 7.6 Hz, 3H), 6.62 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 4H), 6.40–6.32 (m, 2H), 6.24 (dd, *J* = 22.6, 8.6 Hz, 2H), 6.19–6.12 (m, 2H), 3.90 (d, *J* = 7.5 Hz, 6H, 2 × OCH_3), 2.03 (s, 3H, CH_3), 2.01 (m, 2H, CH_2), 1.99(s, 6H, 2 × CH_3), 1.98 (s, 3H, CH_3), 1.74 (s, 3H), 1.66–1.59 (m, 2H), 1.48 (m, 2H, CH_2), 1.04 (s, 6H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.64, 160.27, 146.95, 141.84, 140.29, 137.91, 137.72, 137.66, 137.07, 136.50, 134.20, 133.64, 132.22, 131.64, 131.22, 130.78, 129.63, 129.51, 128.99, 126.96, 125.67, 124.79, 124.27, 103.75, 58.47, 55.84, 39.66, 34.29, 33.14, 29.71, 28.99, 21.78, 19.27, 18.44, 12.90, 12.85, 12.80, 12.75; UV (ethanol) max: 342, 476 nm; HRMS calcd for $C_{42}H_{52}O_3Na$: $[M + Na]^+$: 627.3814; found: 627.3812.

8,12,17,21-Tetramethyl-23-(2,6,6-trimethylcyclohex-1-enyl)-1-phenyltricosa-1,3,6,8,10,12,14,16,18,20,22-undecaen-5-one (**14c**): Yield 81%. m.p. 156–168 °C; IR (KBr): 2923, 1642 (C=O), 1588 (C=C), 1447, 1355, 1257, 1182, 1079 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.29 (m, 8H), 6.97 (d, *J* = 1.9 Hz, 1H), 6.76–6.50 (m, 7H), 6.45 (d, *J* = 15.4 Hz, 1H), 6.40–6.32 (m, 2H), 6.26 (d, *J* = 11.2 Hz, 1H), 6.23–6.09 (m, 3H), 2.02 (m, 2H, CH_2), 2.00 (s, 3H, CH_3), 1.99 (s, 6H, 2 × CH_3), 1.98 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 1.60 (m, 2H, CH_2), 1.49–1.43 (m, 2H, CH_2), 1.04 (s, 6H, 2 × CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 189.00, 147.76, 142.62, 142.53, 141.21, 138.02, 137.96, 137.83, 137.16, 136.70, 136.37, 135.98, 135.72, 134.03, 132.31, 132.00, 130.89, 129.70, 129.65, 129.61, 128.96, 127.35, 127.26, 127.12, 125.89, 124.26, 124.15, 39.77, 34.41, 33.26, 29.84, 29.12, 21.92, 19.39, 14.27, 13.04, 12.93, 12.90, 12.87; UV (ethanol) max: 335, 477 nm; HRMS calcd for $C_{42}H_{51}O$: $[M + H]^+$: 571.3940; found: 571.3941.

Electronic Supplementary Information

The ESI (^{1}H NMR and ^{13}C NMR spectra and the HRMS of β-apo-8'-carotenal (**12**), β-apo-12'-carotenal (**11**), citranaxanthin (**1**) and compounds **13a**–**c** and **14a**–**c**) is available through: stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data

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