

Supplementary Material

A LC-MS profiling method reveals a route for apocarotenes glycosylation and shows its induction by high light stress in Arabidopsis

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Fig. S1. EICs of GAPOs from Arabidopsis by using UHPLC-MS/MS with PRM mode.

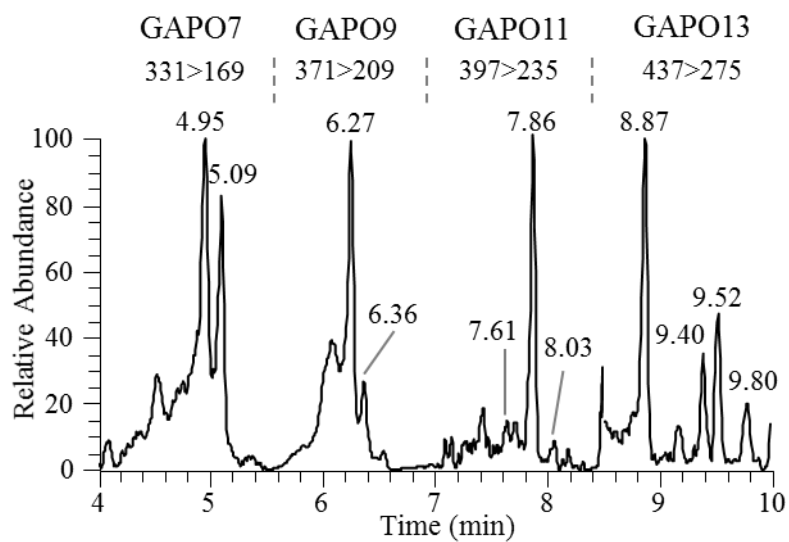


Fig. S2. Optimization of MS parameters including spray voltage (A), auxiliary gas flow rate (B), auxiliary gas heater temperature (C) and sheath gas flow rate (D) for the detection of GAPOs. n = 3, mean \pm SD.

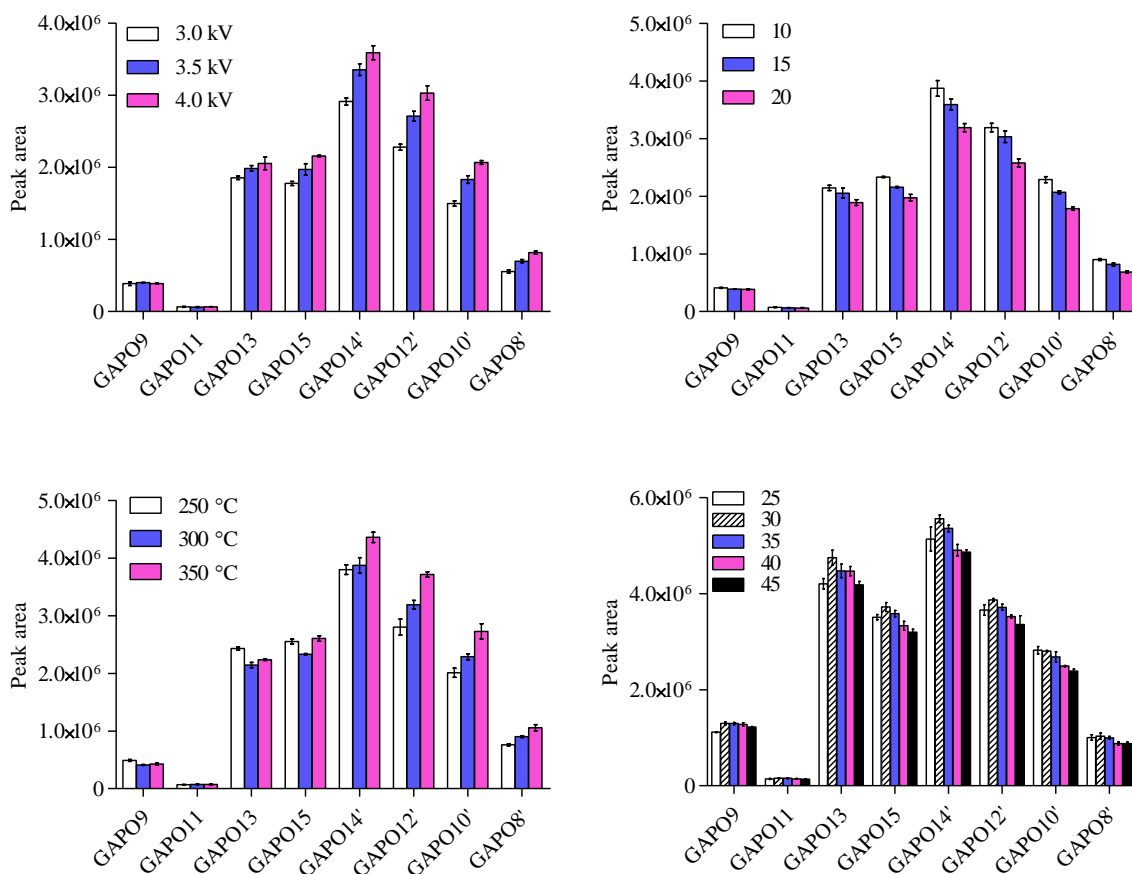


Fig. S3. Identification of Glc- β -cyclocitral and its isomer from Arabidopsis using UHPLC-Q-Orbitrap-MS/MS. (A), HR PRM EICs of Glc-cyclocitral (GAPO7) at ion pair at m/z 331>169 (blue) and D₁-Glc-cyclocitral (D₁-GAPO7) at ion pair at m/z 332>170 (red) from Arabidopsis fed with D₁- β -cyclocitral. (B), HR MS/MS spectra of GA7 at RT 5.09 min (upper) and its isomer GAPO7I at RT 4.95 min (down). The error window is 1 ppm.

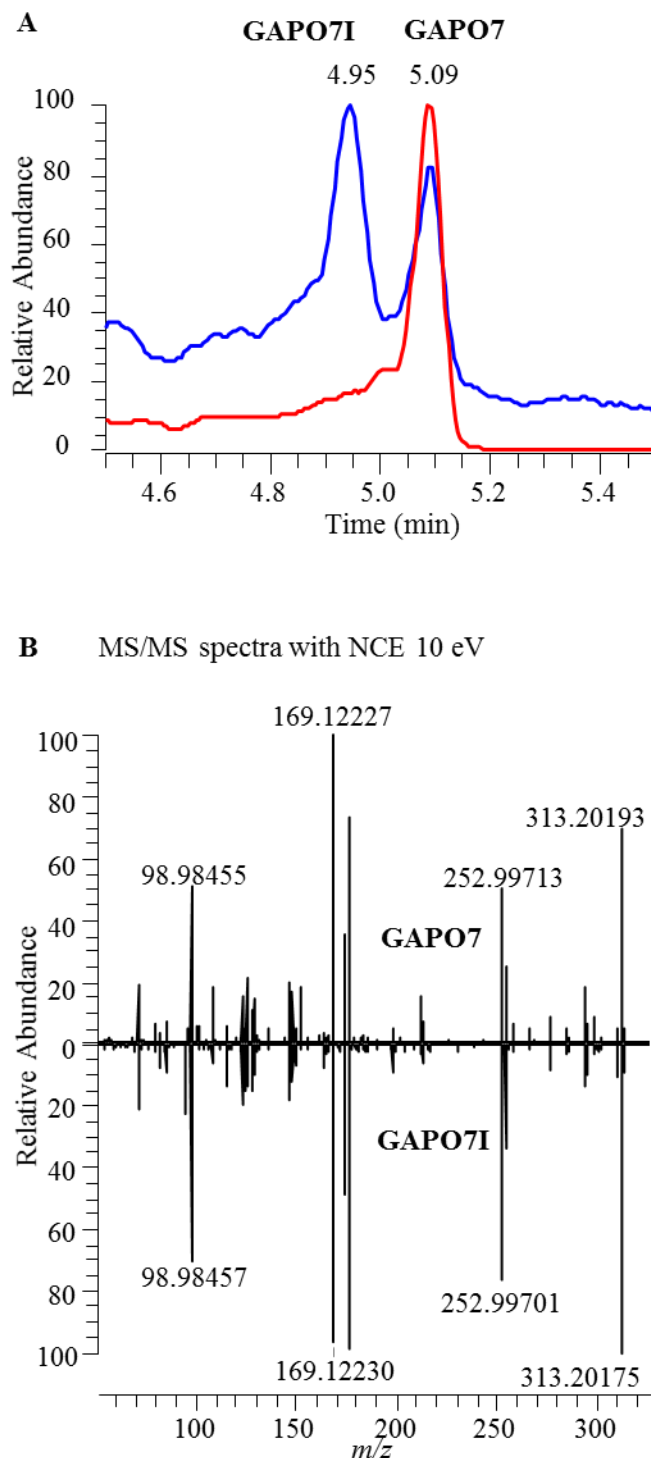


Fig. S4. Confirmation of GAPO9, GAPO11 and their isomers identified from Arabidopsis by the conversion of deuterium-labelled GAPOs from deuterium-labelled apocarotenoids in Arabidopsis (A), HR PRM EICs of GAPO9 and GAPO9I with ion pair at m/z 371>209 from Arabidopsis (black), GAPO9 with ion pair at m/z 371>209 from engineered *E. coli* (blue), and D₃-GAPO9 with ion pair at m/z 374>212 from Arabidopsis fed with D₃- β -ionone (red). (B), (A), HR PRM EICs of GAPO11 and GAPO11I with ion pair at m/z 397>235 from Arabidopsis (black) and engineered *E. coli* (blue), and D₃-GAPO11 and D₃-GAPO11I with ion pair at m/z 400>238 from Arabidopsis fed with D₃- β -apo-11-carotenal (red). The error window is 1 ppm.

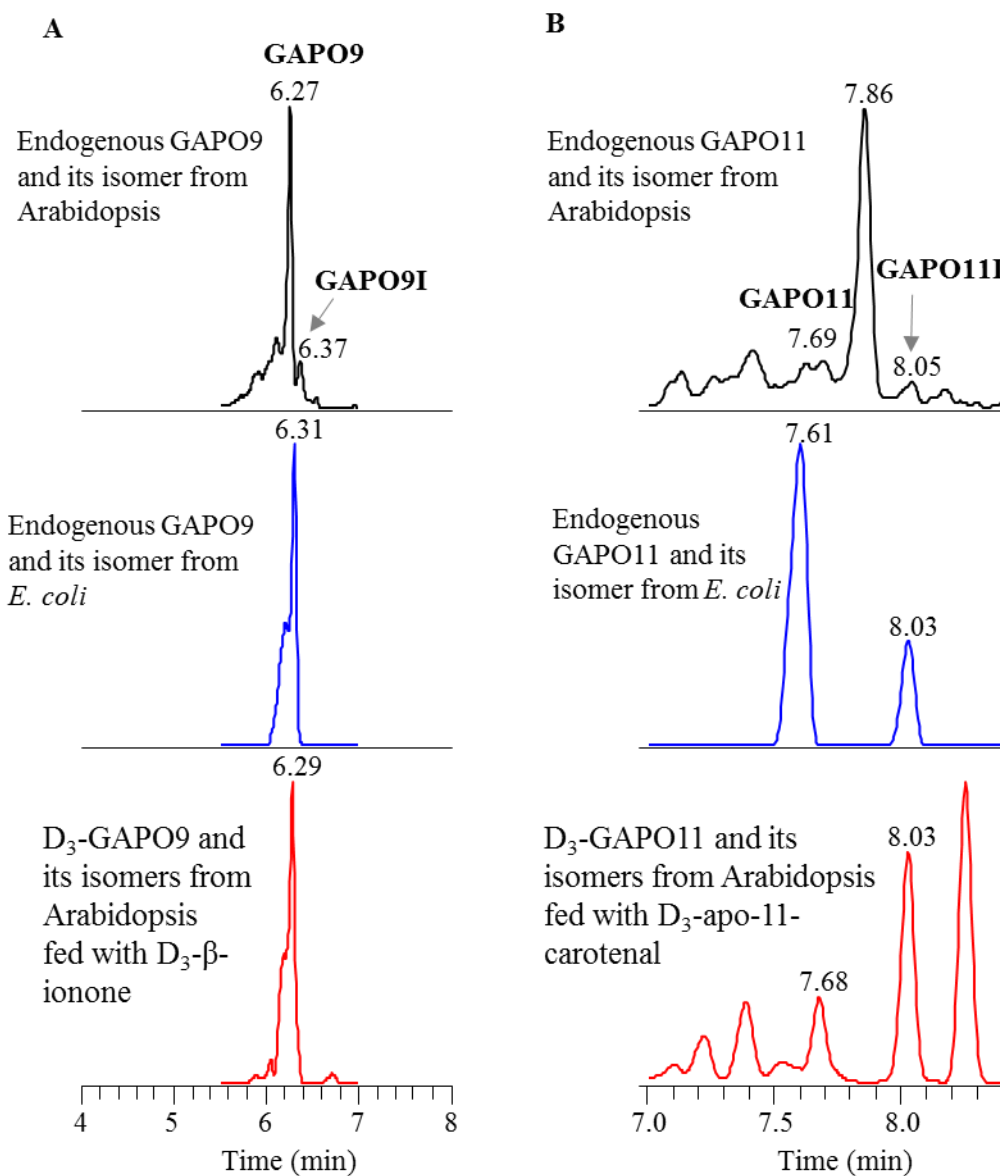


Fig. S5. Chromatographic retention rule of GAPOs on UHPLC C₁₈ column for confirming of the identification of GAPOs from engineered *E.coli* and Arabidopsis. Red dot stands for GAPO7 only found in Arabidopsis at RT 5.09 min and blue dot stands for GAPOs identified in *E. coli* and Arabidopsis. The linear regression formula is inserted.

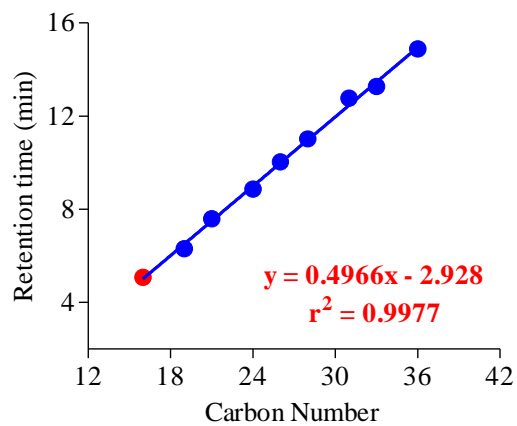


Fig. S6. Quantification of Glc- β -cyclocitral and its isomer from Arabidopsis using UHPLC-HR-MS and UHPLC-HR-MS/MS. HR FS EIC of Glc-cyclocitral at m/z 331.17513 (black) and HR PRM EIC of Glc-cyclocitral at ion pair at m/z 331>169 (blue) from Arabidopsis. The error window is 1 ppm.

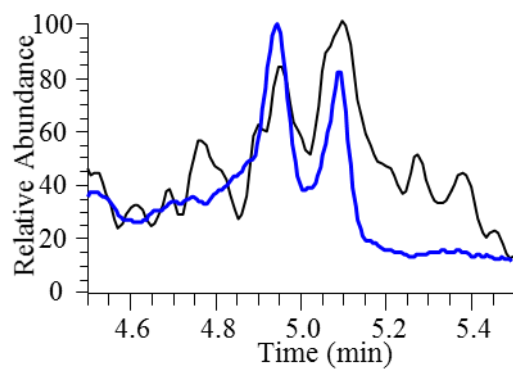


Table S1. Identification of GAPOs from zeaxanthin diglucoside accumulating *E. coli* cells and**Arabidopsis.**

Name	RT (min)	Formula	Experimental [M+H] ⁺ (<i>m/z</i>)	Theoretical [M+H] ⁺ (<i>m/z</i>)	Error (ppm)	MS/MS (<i>m/z</i>)
GAPO7	5.09	C ₁₆ H ₂₆ O ₇	311.17493	331.17513	-0.61	169.12222
GAPO7I	4.95	C ₁₆ H ₂₆ O ₇	311.17480	331.17513	-0.98	169.12216, 151.11176
GAPO9	6.31	C ₁₉ H ₃₀ O ₇	371.20636	371.20643	-0.19	209.15349, 191.14294, 173.13243
GAPO9I	6.37	C ₁₉ H ₃₀ O ₇	371.20609	371.20643	-0.93	209.15337, 191.14282, 173.13232
GAPO11	7.61	C ₂₁ H ₃₂ O ₇	397.22189	397.22208	-0.47	235.16902
GAPO11I	8.03	C ₂₁ H ₃₂ O ₇	397.22174	397.22208	-0.85	235.16924
GAPO13	8.88	C ₂₄ H ₃₆ O ₇	437.25391	437.25338	-0.40	275.20053, 257.18973, 173.13223
GAPO13I	9.41	C ₂₄ H ₃₆ O ₇	437.25342	437.25338	0.07	275.20044
GAPO13II	9.51	C ₂₄ H ₃₆ O ₇	437.25348	437.25338	0.09	275.20053, 257.18982, 173.13176
GAPO13III	9.80	C ₂₄ H ₃₆ O ₇	437.25340	437.25338	0.05	275.20029
GAPO15	10.03	C ₂₆ H ₃₈ O ₇	463.26895	463.26903	-0.17	301.21603, 283.20532, 173.13246
GAPO15I	10.47	C ₂₆ H ₃₈ O ₇	463.26901	463.26903	-0.04	301.21606, 283.20544, 173.13245
GAPO14'	11.03	C ₂₈ H ₄₀ O ₇	489.28470	489.28468	0.04	327.23160, 309.22101, 173.13219
GAPO14'I	11.61	C ₂₈ H ₄₀ O ₇	489.28473	489.28468	0.10	327.23160, 309.22147
GAPO14'II	11.70	C ₂₈ H ₄₀ O ₇	489.28473	489.28468	0.10	327.23178, 309.22098
GAPO12'	12.77	C ₃₁ H ₄₄ O ₇	529.31635	529.31598	0.69	367.26294, 349.25223, 173.13237
GAPO12'I	13.62	C ₃₁ H ₄₄ O ₇	529.31641	529.31598	0.81	367.26306, 349.25259
GAPO12'II	13.82	C ₃₁ H ₄₄ O ₇	529.31641	529.31598	0.81	367.26297, 349.25137
GAPO10'	13.27	C ₃₃ H ₄₆ O ₇	555.33179	555.33163	0.28	393.27853, 375.26791, 173.13271
GAPO10'I	14.24	C ₃₃ H ₄₆ O ₇	555.33179	555.33163	0.28	393.27832, 375.26758
GAPO10'II	14.53	C ₃₃ H ₄₆ O ₇	555.33191	555.33163	0.50	393.27844, 375.26743
GAPO8'	14.88	C ₃₆ H ₅₀ O ₇	595.36340	595.36293	0.79	433.31003, 415.29901, 173.13277
GAPO8'I	16.11	C ₃₆ H ₅₀ O ₇	595.36262	595.36293	-0.97	433.31039, 415.29868
GAPO8'II	16.25	C ₃₆ H ₅₀ O ₇	595.36292	595.36293	-0.03	433.30963, 415.30011
GAPO8'III	16.44	C ₃₆ H ₅₀ O ₇	595.36328	595.36293	0.59	433.31024, 415.29816