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 ± 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 C\textsubscript{18} column for confirming of the identification of GAPOs from engineered \textit{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 \textit{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.

<table>
<thead>
<tr>
<th>Name</th>
<th>RT (min)</th>
<th>Formula</th>
<th>Experimental [M+H]+ (m/z)</th>
<th>Theoretical [M+H]+ (m/z)</th>
<th>Error (ppm)</th>
<th>MS/MS (m/z)</th>
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