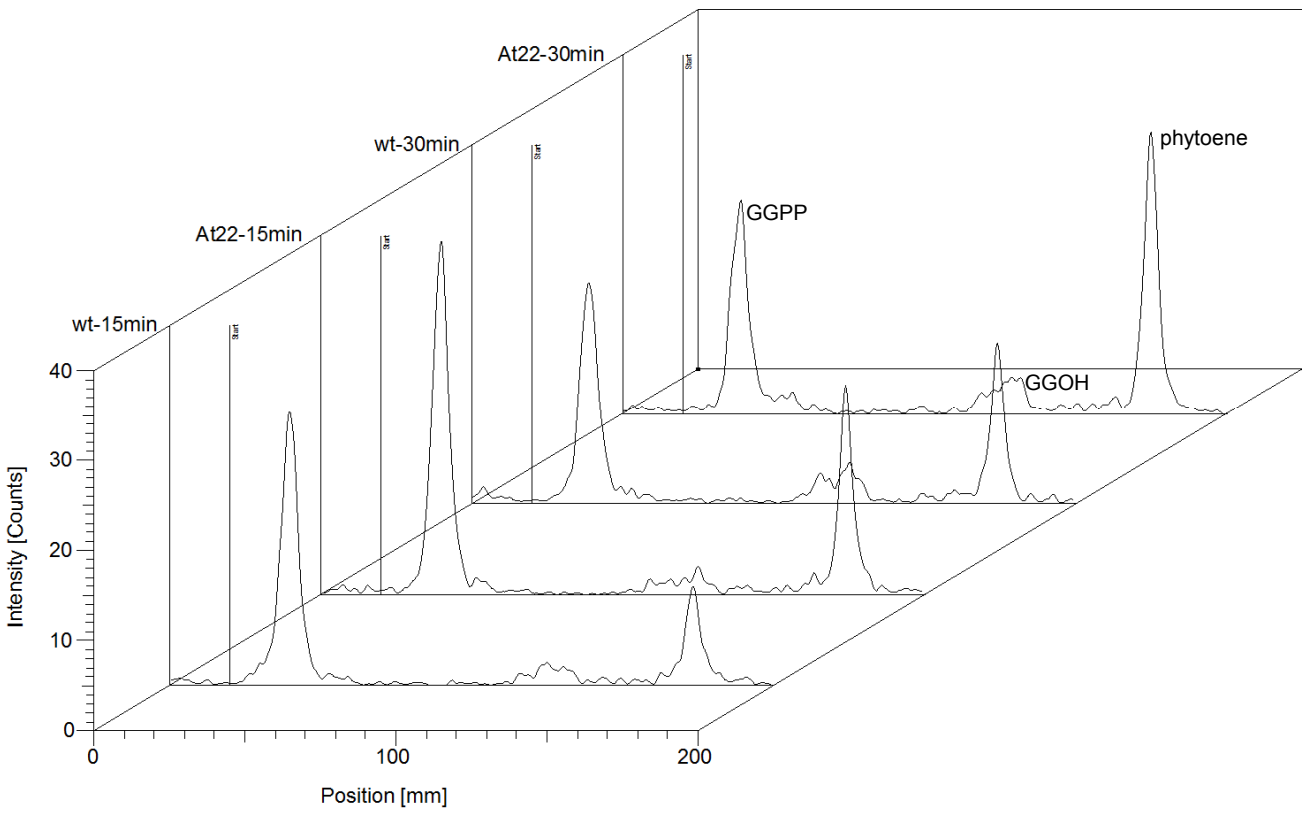
Supplemental Table I

apocarotenoid	fragmentation (m/z)	RT (min)	KI	possible precursors
3-oxo-α-ionol (apo1)	208 ($M^{\bullet+}$), 108 (100), 152	9.02	1653	L, aC, bC, Zo, Z, A
3-oxo-α-ionone (apo2)	206 ($M^{\bullet+}$), 108 (100), 150	9.05	1656	L, aC, bC, Zo, Z, A
3-hydroxy-5,6-epoxy-β-ionone (apo3)	224 ($M^{\bullet+}$), 123, (100)	9.20	1671	V, N, A
6-hydroxy-3-oxo-β-ionone (apo4)	222 ($M^{\bullet+}$), 124 (100), 166	9.74	1829	V, N, A

Supplemental Table I: Characteristics of apocarotenoid aglycons identified in Arabdiopsis leaves.

Molecule ions (M•+) and major fragments are given; the main fragment is indicated by (100); KI, non-isothermal Kovats retention index; RT, retention time; possible precursor xanthophylls are indicated: L, lutein, aC, α-cryptoxanthin, bC, β-cryptoxanthin, Zo, zeinoxanthin, Z, zeaxanthin, A, antheraxanthin, V, violaxanthin, N, neoxanthin.

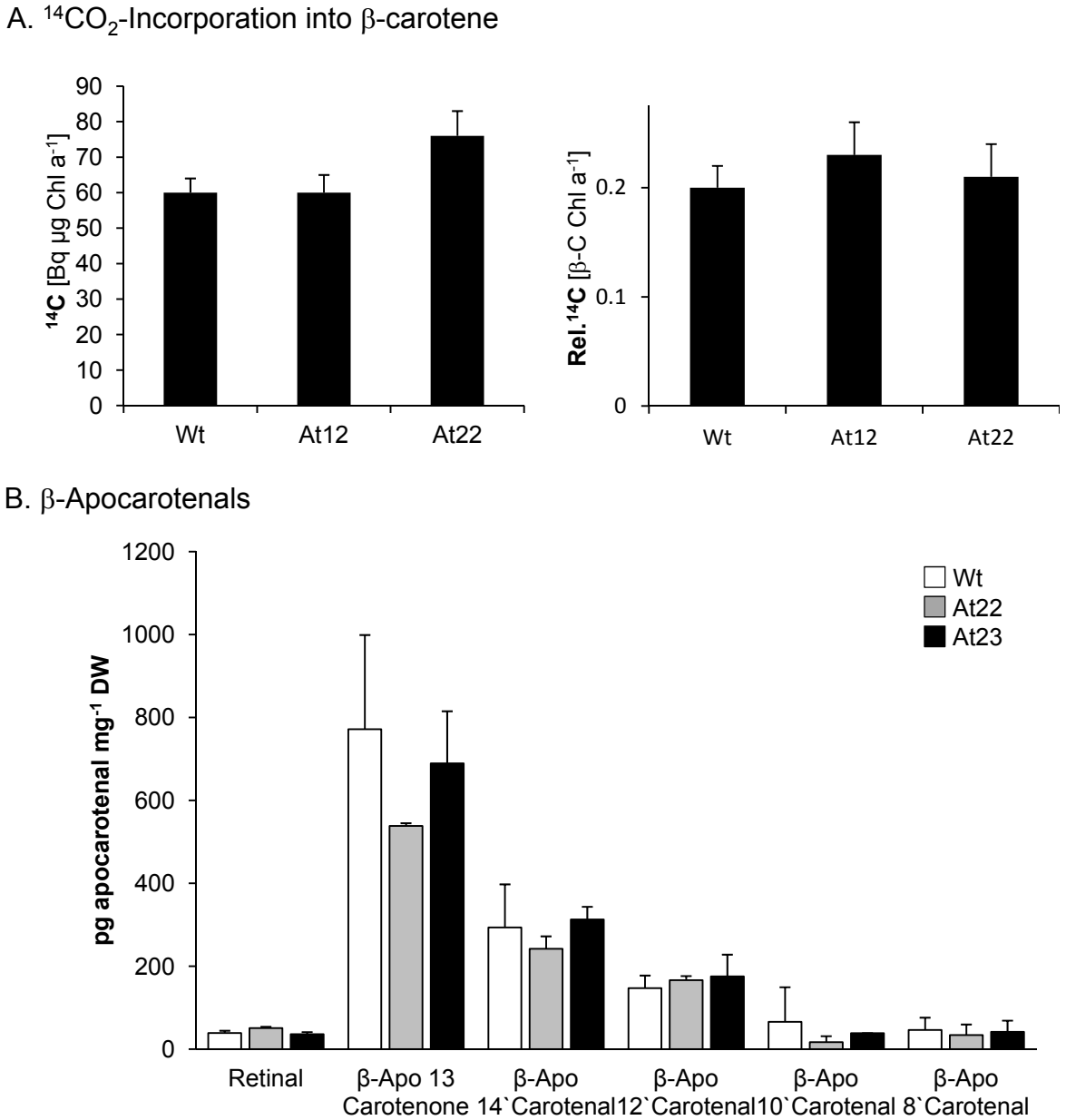
Supplemental Figure 1



Supplemental Figure 1: [^{14}C]-labelled compounds formed in an *in vitro* PSY activity assay

Chloroplast membranes were incubated with mustard GGPP synthase, DMAPP and [^{14}C]IPP for 15 and 30 min, respectively. Chloroform extracts were separated by TLC and analyzed by TLC scanning. The following components were identified: GGPP (40 mm), GGOH (140 mm) and phytoene (170 mm). Wt, wild type, At22, *AtPSY*-overexpressing line

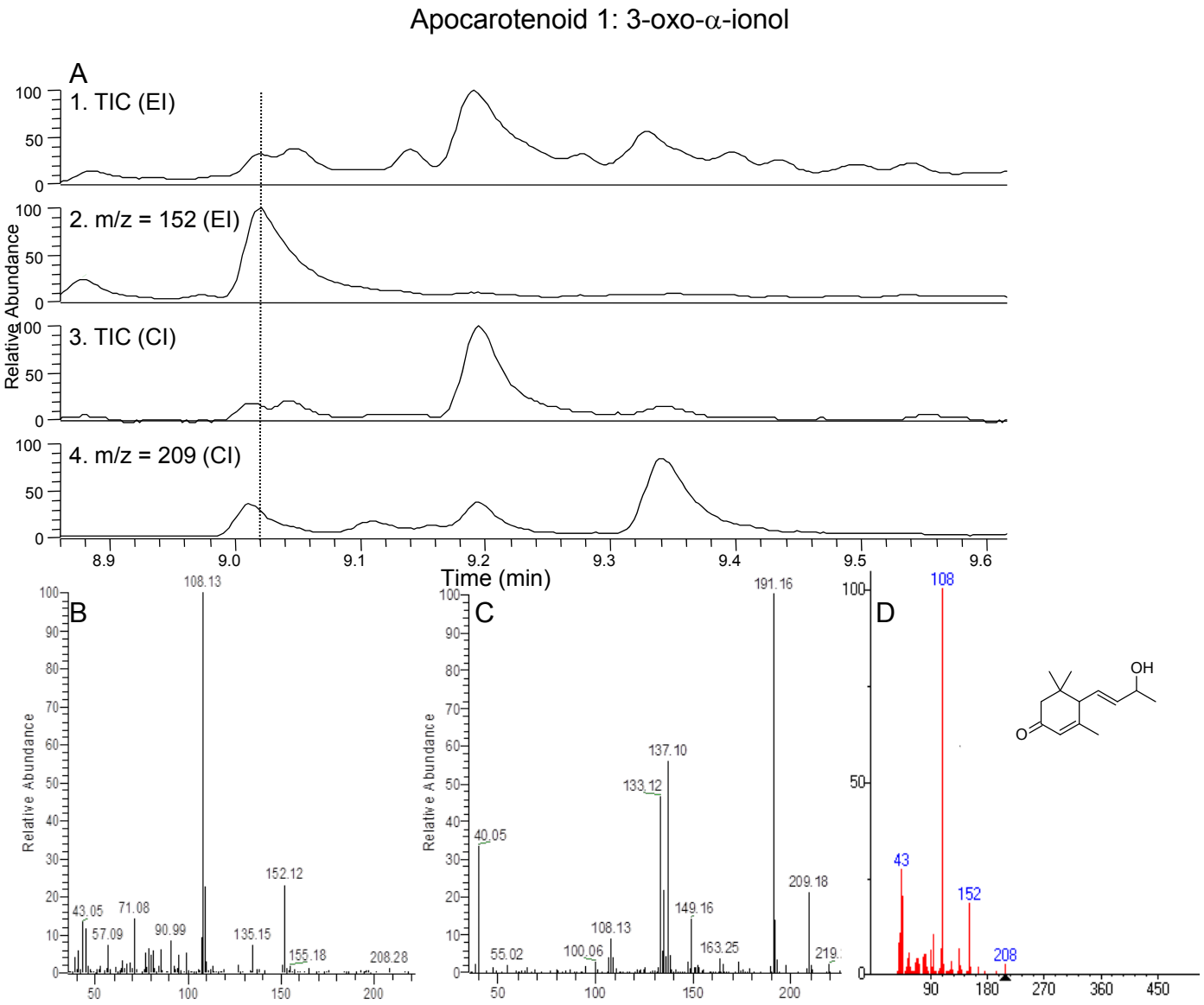
Supplemental Figure 2



Supplemental Figure 2: β-Apocarotenoids in Arabidopsis leaves

A) $^{14}CO_2$-Incorporation into b-carotene in leaves from wild-type and *AtPSY*-overexpressing lines upon pulse-chase labeling (At12, At22). Amounts of ^{14}C-β-carotene are expressed relative to the chlorophyll a content (left) and to the incorporation of ^{14}C into Chl a (right).
B) β-Carotene derived apocarotenoids were analyzed in leaves from 4-week-old plants from Arabidopsis wild type (ecotype Wassilewskija, Wt) and two *AtPSY*-overexpressing lines (At22 and At23). Apocarotenal/one amounts were quantified according to external standards and expressed in pg per mg dry weight. Data are mean ± SE of three biological replicates. No significant differences were detected (Student's *t* test, $p > 0.1$)

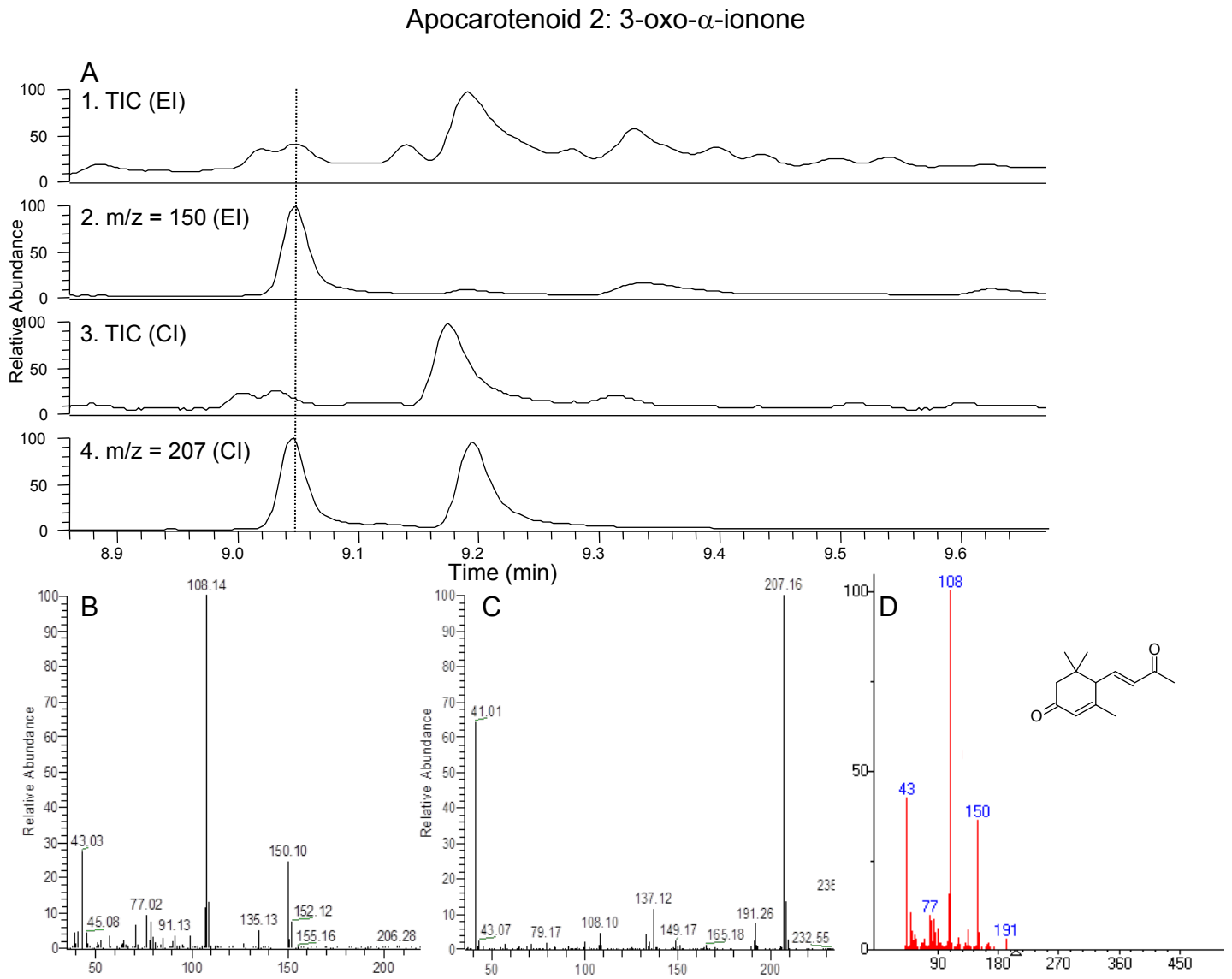
Supplemental Figure 3



Supplemental Figure 3: Identification of 3-oxo-α-ionol in glycosidase-digested Arabidopsis wild-type leaf extracts by GC-MS analysis.

A, total ion current (TIC) chromatogram of extracts run in electron impact ionization mode (EI, 1); 3-oxo-α-ionol was clearly identifiable at a retention time of 9.02 +/- 0.02 min upon scanning for its fragment of m/z = 152 (2). For confirmation, extracts were run in chemical ionization mode (CI). This revealed both in TIC (3) as well as upon scanning for its pseudo-molecular ion of m/z = $[M+H]^+$ = 209 a specific peak at identical retention time (4). Mass spectra of 3-oxo-α-ionol upon EI (B), CI (C) and from the database (D) are also shown.

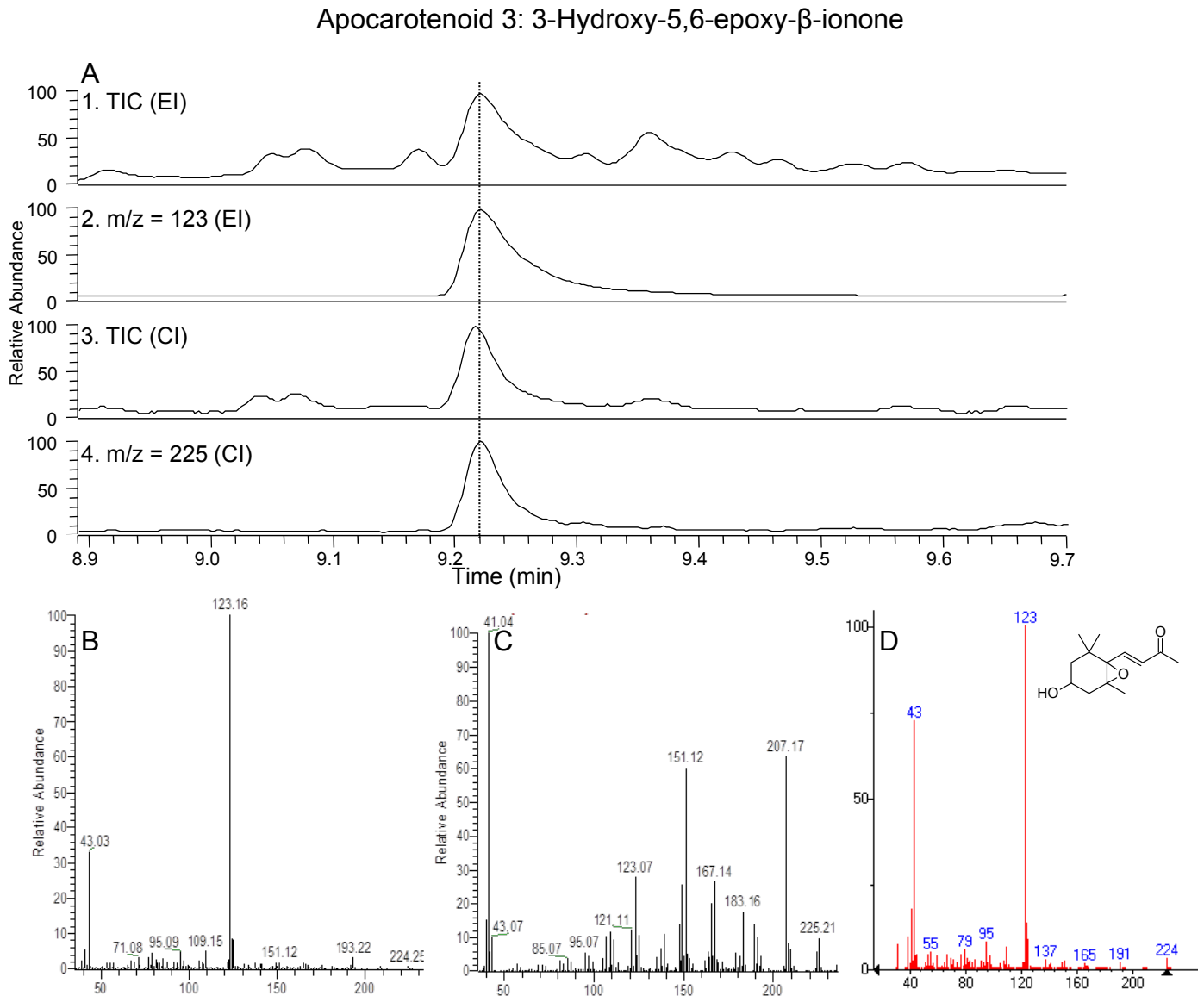
Supplemental Figure 4



Supplemental Figure 4: Identification of 3-oxo-α-ionone in glycosidase-digested Arabidopsis wild-type leaf extracts by GC-MS analysis.

A, total ion current (TIC) chromatogram of extracts run in electron impact ionization mode (EI, 1); 3-oxo-α-ionone was clearly identifiable at a retention time of 9.05 +/- 0.02 min upon scanning for its fragment of m/z = 150 (2). For confirmation, extracts were run in chemical ionization mode (CI). This revealed both in TIC (3) as well as upon scanning for its pseudo-molecular ion of m/z = $[M+H]^+$ = 207 a specific peak at identical retention time (4). Mass spectra of 3-oxo-a-ionone upon EI (B), CI (C) and from the database (D) are also shown.

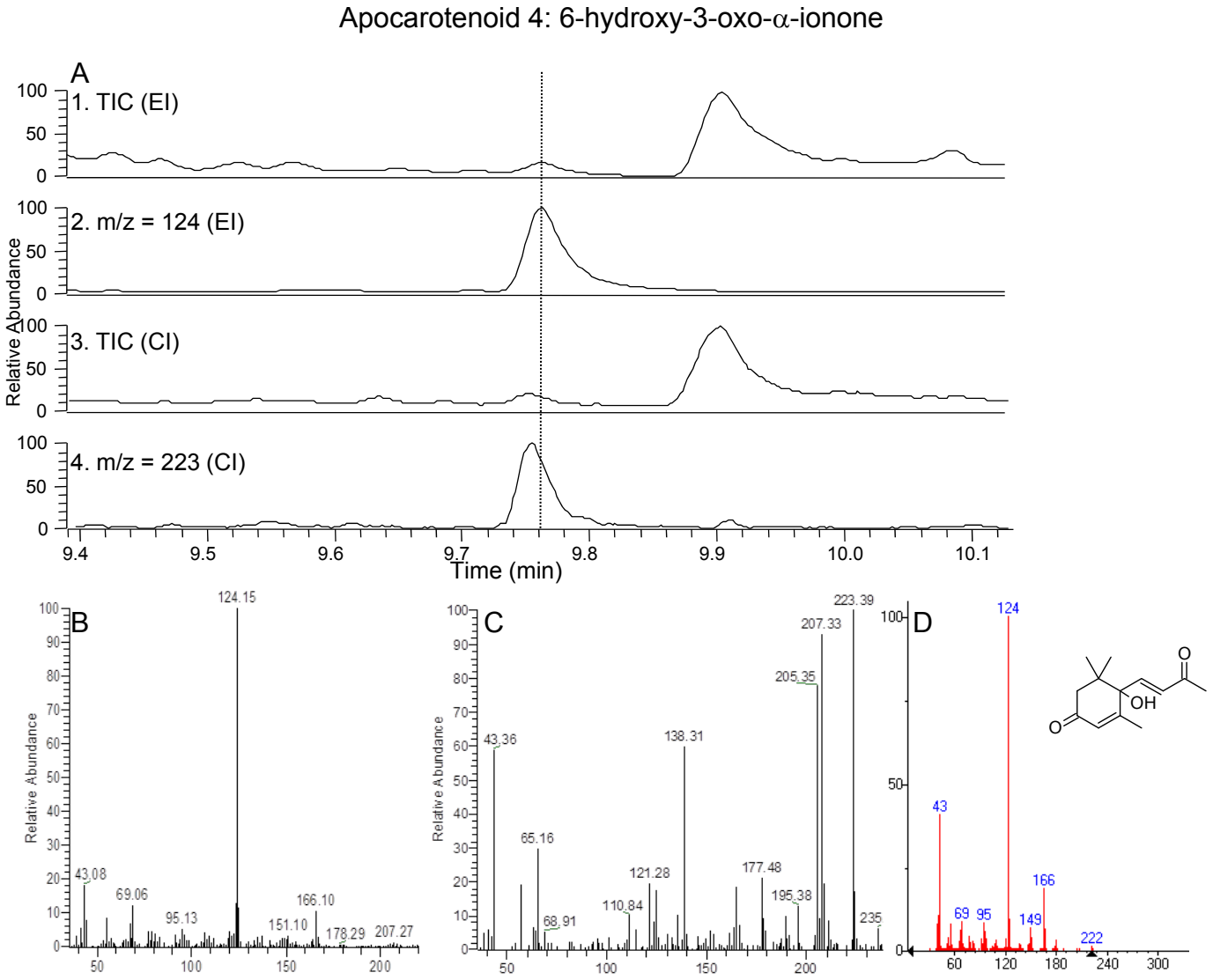
Supplemental Figure 5



Supplemental Figure 5: Identification of 3-hydroxy-5,6-epoxy-β-ionone in glycosidase-digested Arabidopsis wild-type leaf extracts by GC-MS analysis.

A, total ion current (TIC) chromatogram of extracts run in electron impact ionization mode (EI, 1); 3-Hydroxy-5,6-epoxy-β-ionone was clearly identifiable at a retention time of 9.24 +/- 0.02 min upon scanning for its main fragment of m/z = 123 (2). For confirmation, extracts were run in chemical ionization mode (CI). This revealed both in TIC (3) as well as upon scanning for its pseudo-molecular ion of m/z = $[M+H]^+$ = 225 a specific peak at identical retention time (4). Mass spectra of 3-hydroxy-5,6-epoxy-β-ionone upon EI (B), CI (C) and from the database (D) are also shown.

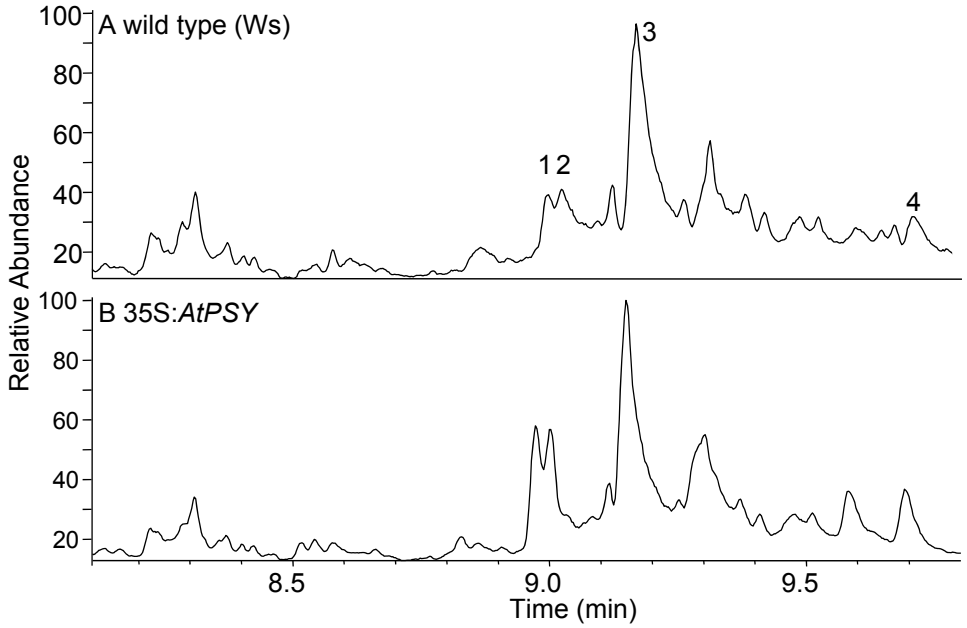
Supplemental Figure 6



Supplemental Figure 6: Identification of 6-hydroxy-3-oxo-α-ionone in glycosidase-digested Arabidopsis wild-type leaf extracts by GC-MS analysis.

A, total ion current (TIC) chromatogram of extracts run in electron impact ionization mode (EI, 1); 6-hydroxy-3-oxo-α-ionone was clearly identifiable at a retention time of 9.74 +/- 0.02 min upon scanning for its main fragment of m/z = 124 (2). For confirmation, extracts were run in chemical ionization mode (CI). This revealed both in TIC (3) as well as upon scanning for its pseudo-molecular ion of m/z = $[M+H]^+$ = 223 a specific peak at identical retention time (4). Mass spectra of 6-hydroxy-3-oxo-α-ionone upon EI (B), CI (C) and from the database (D) are also shown.

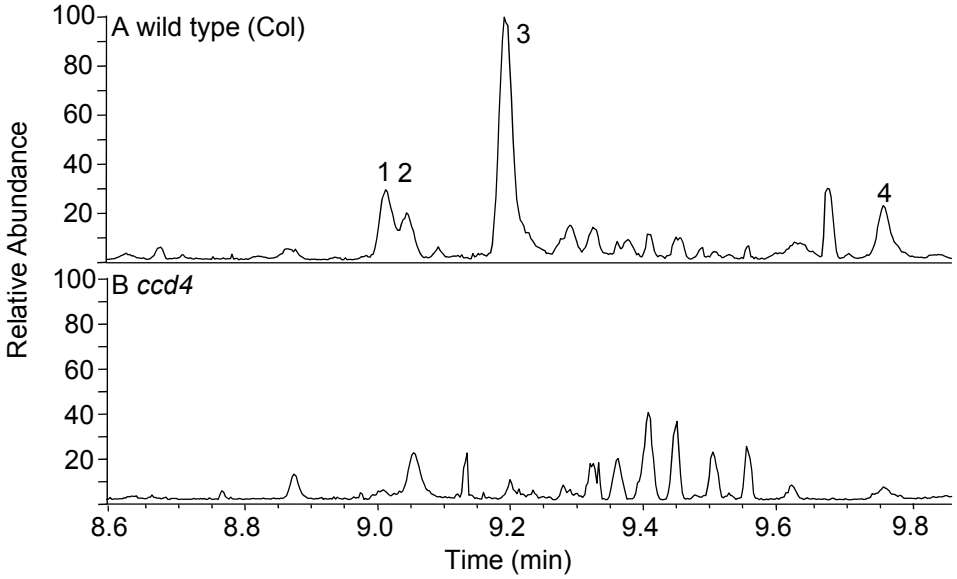
Supplemental Figure 7



Supplemental Figure 7: Apocarotenoid glycosides in *AtPSY*-overexpressing Arabidopsis leaves

Hydrophilic leaf extracts from Arabidopsis wild-type (ecotype Wassilewskija; A) and *AtPSY*-overexpressing line At23 (B) were digested with glycosidase, extracted with pentane and analyzed by GC-MS. Backgrounds from corresponding non-digested samples were subtracted and total ion current chromatograms between 8.2 and 9.8 min run time are shown. Apocarotenoids were identified as follows: 1, 3-oxo-α-ionol, 2, 3-oxo-α-ionone, 3, 3-hydroxy-5,6-epoxy-β-ionone and 4, 6-hydroxy-3-oxo-α-ionone.

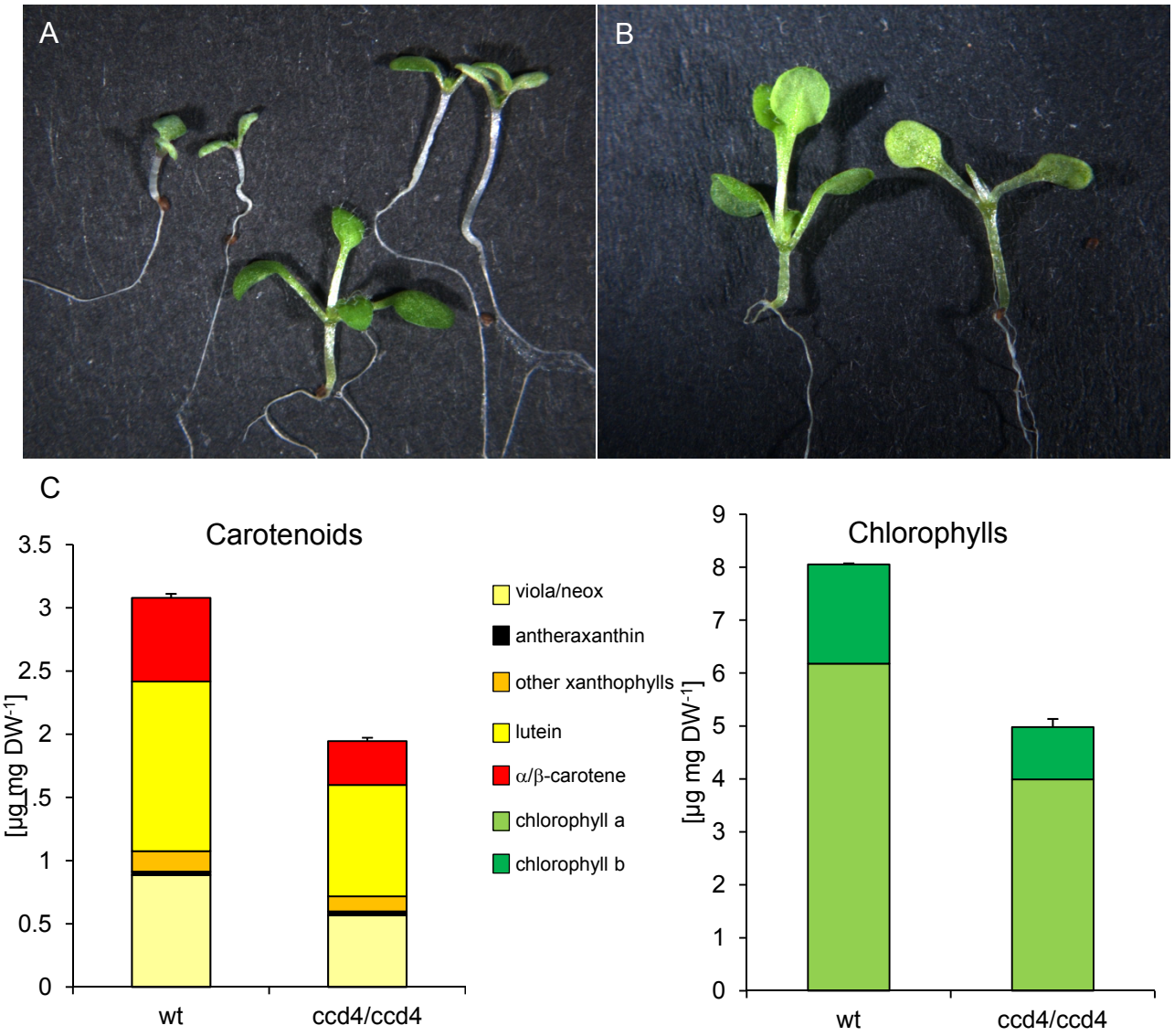
Supplemental Figure 8



Supplemental Figure 8: Apocarotenoid glycosides in leaves from Arabidopsis *CCD4* mutant

Hydrophilic leaf extracts from Arabidopsis wild-type (ecotype Columbia, col, A) and CCD4 (B) mutant plants were digested with glycosidase, extracted with pentane and analyzed by GC-MS. Backgrounds from corresponding non-digested samples were subtracted and total ion current chromatograms between 8.6 and 9.8 min run time are shown. Apocarotenoids were identified as follows: 1, 3-oxo-α-ionol, 2, 3-oxo-α-ionone, 3, 3-hydroxy-5,6-epoxy-β-ionone and 4, 6-hydroxy-3-oxo-α-ionone.

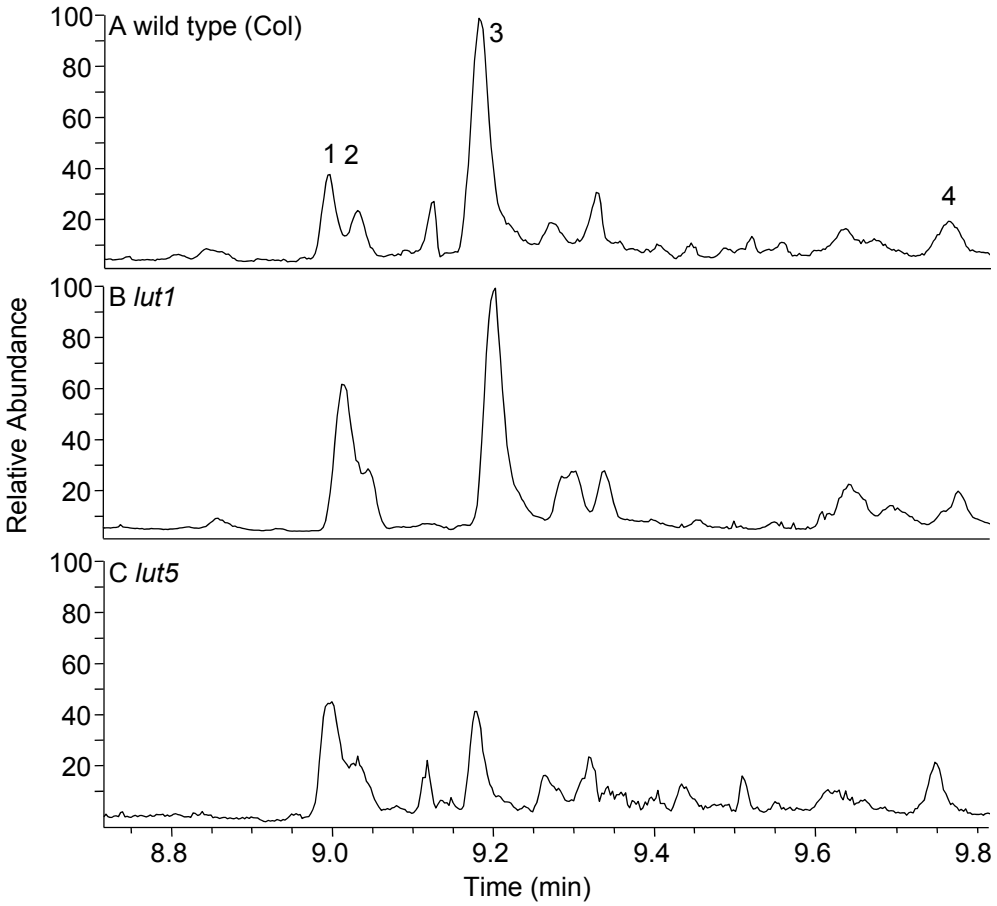
Supplemental Figure 9



Supplemental Figure 9: Crosses between *AtPSY*-overexpressing and *ccd4-1* mutant Arabidopsis line

One *AtPSY*-overexpressing line was crossed with the *ccd4-1* mutant. Seeds from the F3 generation homozygous for the *35S:AtPSY* transgene were germinated on MS agar for one week. A) Seedlings homozygous for the *ccd4-1* mutation developed bleached cotyledons both under control light (100 µmol photons m^{-2} s^{-1}; left) and low light (10 µmol photons m^{-2} s^{-1}; right). B) Although development of primary leaves was initiated they did not develop further (right) and the plants died. Wt seedlings grown in parallel are shown as control. C) HPLC analyses of one week old seedlings grown under control light revealed about 40 % reduced levels of both carotenoids and chlorophylls compared to the wild type. Data are mean ± SE of three biological (wt) and two technical (*ccd4/ccd4*) replicates.

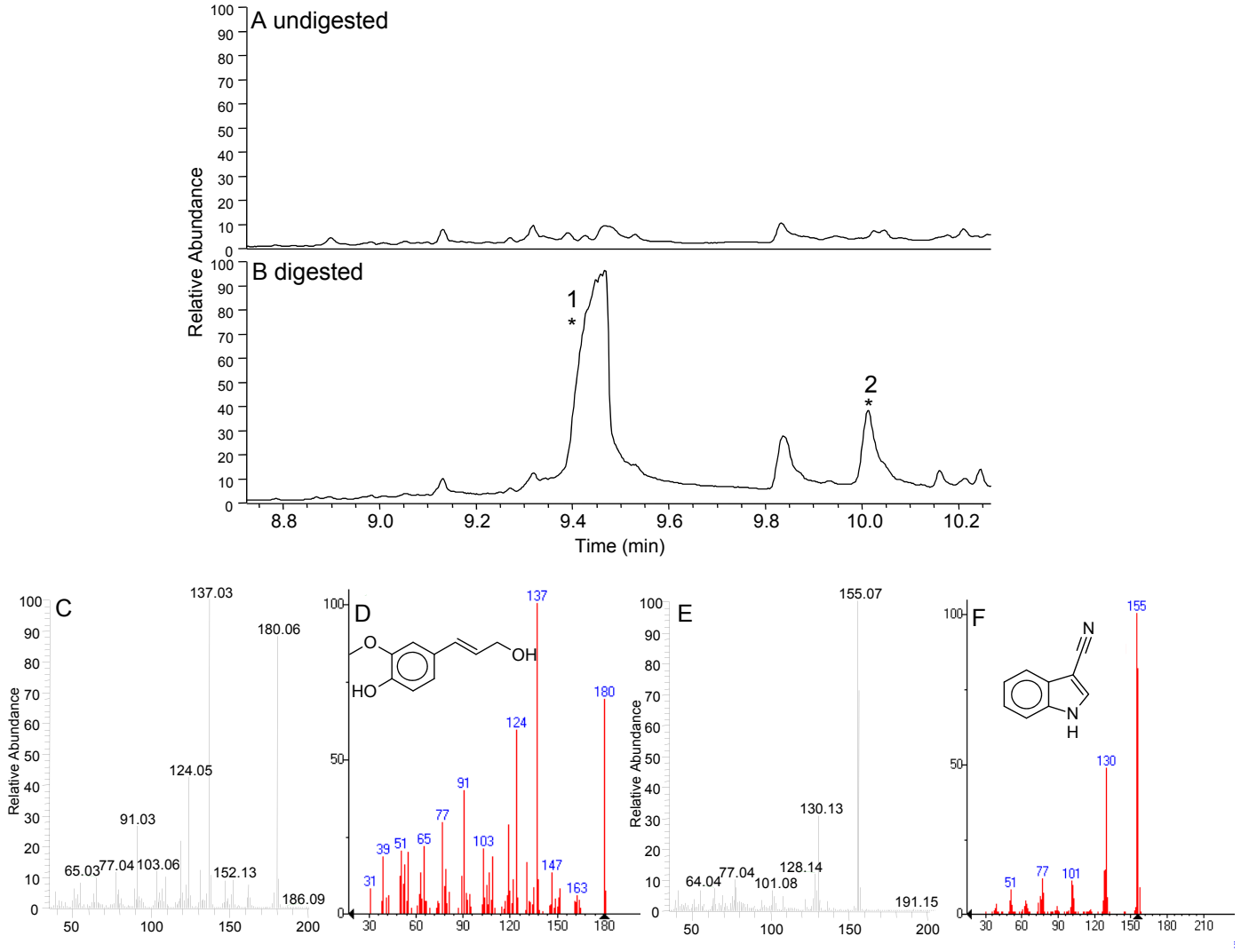
Supplemental Figure 10



Supplemental Figure 10: Apocarotenoid aglycons in leaves from Arabidopsis carotene hydroxylase mutants

Hydrophilic leaf extracts from Arabidopsis wild-type (ecotype Columbia; col, A), *lut1* (B) and *lut5* (C) mutant plants were digested with glycosidase, extracted with pentane and analyzed by GC-MS. Backgrounds from corresponding non-digested samples were subtracted and total ion current chromatograms between 8.6 and 9.8 min run time are shown. Apocarotenoids were identified as follows: 1, 3-oxo-α-ionol, 2, 3-oxo-α-ionone, 3, 3-hydroxy-5,6-epoxy-β-ionone and 4, 6-hydroxy-3-oxo-α-ionone.

Supplemental Figure 11



Supplemental Figure 11: Identification of coniferyl alcohol and indol-3-acetonitril in glycosidase-digested Arabidopsis wild-type root extracts by GC-MS analysis

Total ion current chromatogram of extracts run in electron impact ionization mode before (A) and after digestion with glycosidase (B). C, Recorded mass spectra of coniferyl alcohol at RT 9.42 (peak 1) and E, indol-3-acetonitril at RT 10.0 (peak 2) and those retrieved from the database (D and F, respectively) are also shown.