

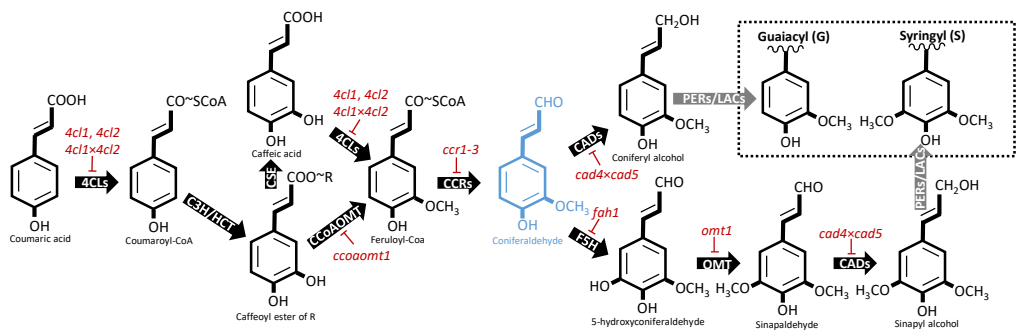
# ChemSusChem

Supporting Information

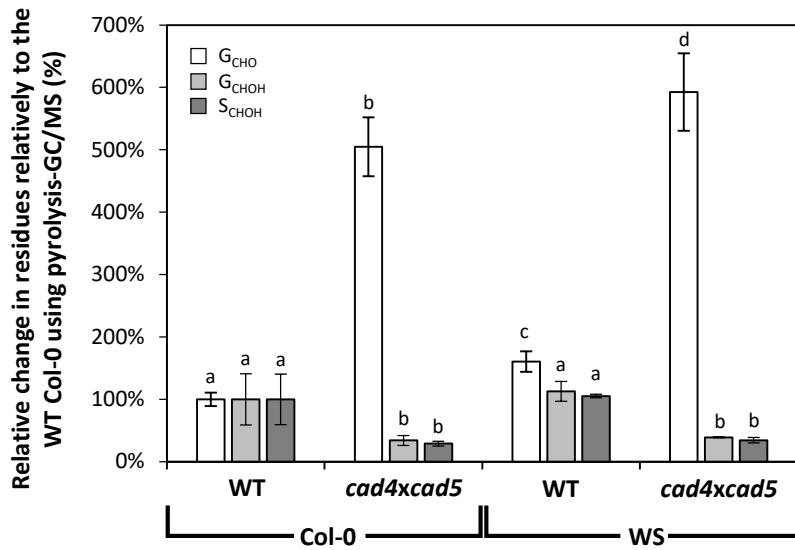
## **Importance of Lignin Coniferaldehyde Residues for Plant Properties and Sustainable Uses**

Masanobu Yamamoto, Leonard Blaschek, Elena Subbotina, Shinya Kajita, and Edouard Pesquet\* © 2020 The Authors. Published by Wiley-VCH GmbH.

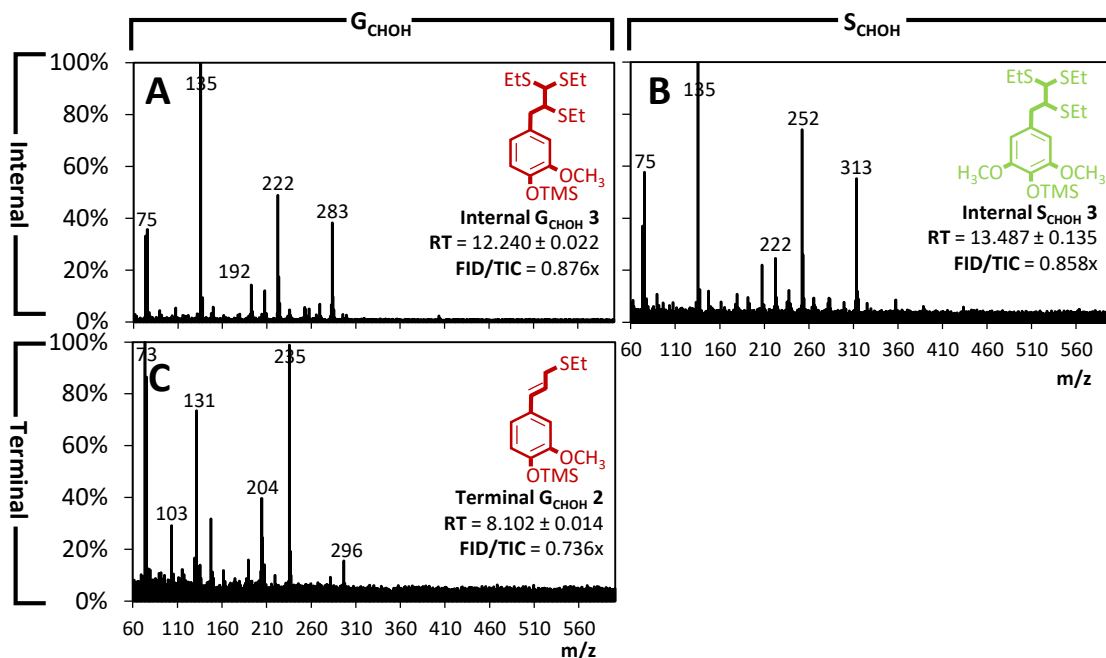
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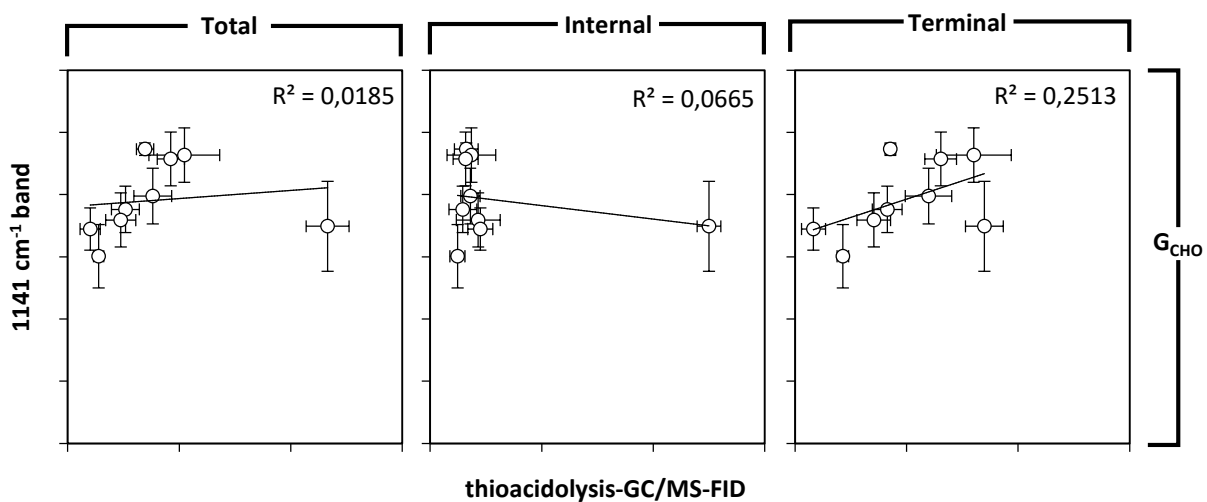
**Figure S1.** Schematic representation of conventional lignin monomer biosynthesis (black arrows) and polymerization (grey arrows) processes. Note that mutants used in this study are presented in red for 4-COUMARATE:CoA LIGASEs (4CLs), CAFFEOYL-CoA *O*-METHYLTRANSFERASE 1 (CCoAOMT1), CINNAMOYL-CoA REDUCTASEs (CCRs), CINNAMYL ALCOHOL DEHYDROGENASEs (CADs), FERULATE-5 HYDROXYLASE (F5H), *O*-METHYLTRANSFERASE (OMT). Other important step in lignin formation include COUMARATE-3-HYDROXYLASE and SHIKIMATE/QUINATE HYDROXYCOUMAROYLTRANSFERASE (C3H/HCT), CAFFEOYL-SHIKIMATE ESTERASE (CSE), PEROXIDASEs (PERs) AND LACCASEs (LACs). Note that coniferaldehyde is indicated in blue.



**Figure S2.** Influence of natural diversity on the proportion of coniferaldehyde ( $G_{CHO}$ ), coniferyl alcohol ( $G_{CHOH}$ ) and sinapyl alcohol ( $S_{CHOH}$ ) in lignin of *Arabidopsis* stem tissues using pyrolysis-GC/MS. Data is expressed as a percentage of wild-type (WT) plants of the Columbia 0 (Col-0) background for each residue compared to Wassilewskija (WS) and/or *cad4xcad5* mutations (n = 3 independent biological replicates per genotype). Different letters for each residue category indicate significant differences using one-way ANOVA with Tukey test.



**Figure S3.** Diagnostic thioacidolysed compounds deriving from terminal and internal residues of coniferyl alcohol ( $G_{CHOH}$ ) and sinapyl alcohol ( $S_{CHOH}$ ) in cell walls of stem tissues. Characteristics of diagnostic compound are presented for internal (A-B) and terminal (C) residues of  $G_{CHOH}$  (A,C) and  $S_{CHOH}$  (B) by their  $m/z$ <sup>[40-45]</sup>, retention time (RT in min) and FID/TIC ratio.



**Figure S4.** Linear correlation analyses between the 1141 cm<sup>-1</sup> Raman band height and thioacidolysis-GC/MS-FID for coniferaldehyde (G<sub>CHO</sub>) residues connected by ether C-O-C linkages at different position with the lignin polymers of stem tissues in a set of *Arabidopsis* with modified lignins.