Laccase Specificity Determines Lignin Composition

Background

- In contrast to the heterogeneity and cross-linking found in classical lignin polymers, catechyl (C) lignin is a linear homopolymer of caffeyl alcohol which greatly simplifies its conversion to industrial chemicals. Yet, the factors controlling C-lignin biosynthesis remain unclear.

Approach

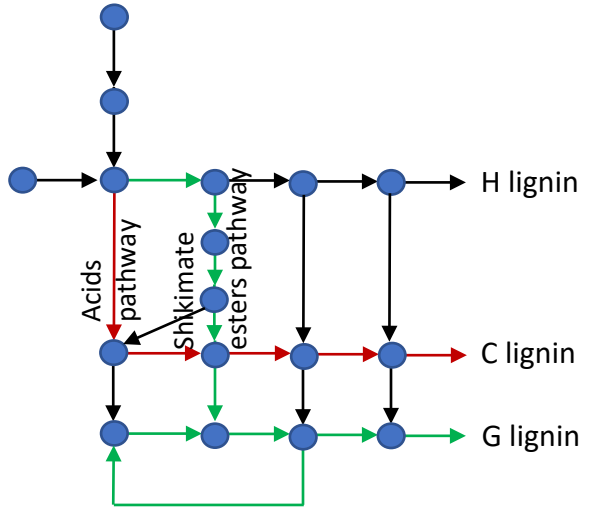
- *Cleome hassleriana* is excellent model system to interrogate the molecular mechanisms underlying C-lignin biosynthesis because lignin composition in seed coats changes from guaiacyl (G) lignin to C-lignin at around 12-14 days after pollination (DAP).
- A combination of metabolite profiling, isotopic labeling analyses, metabolic flux analysis, and enzyme specificity studies were used to determine the origin, levels, and fates of the precursor pools for lignin biosynthesis during the development of the *Cleome* seed coat.

Results

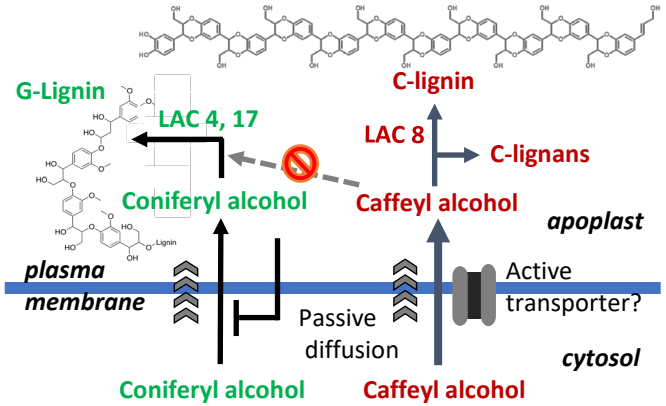
- C-lignin biosynthesis proceeds when coniferyl alcohol (G monolignol) is still being formed.
- Monolignol supply is not itself sufficient to determine lignin composition.
- Caffeyl alcohol inhibits the oxidation of coniferyl alcohol by *Cleome* seed coat cell wall laccases to ensure C-homopolymer biosynthesis at late stages of seed coat development.
- LACCASE8 from *Cleome* has the unusual property of oxidizing caffeyl alcohol but not coniferyl alcohol.

Significance

- A simple mechanism based on passive diffusion of coniferyl alcohol, coupled with laccase specificity, accounts for the metabolic fates of G and C monolignols in the *Cleome* seed coat. The inhibition of coniferyl alcohol polymerization by caffeyl alcohol explains how it is possible to form an independent C-homopolymer in the presence of coniferyl alcohol.
- These insights may allow higher C-lignin production in other more commercial plant tissues.



Metabolic flux analysis reveals different routes to monolignols during the phases of G- and C-lignin synthesis



A model for the control of lignin composition in the *Cleome* seed coat based on substrate availability, transport and polymerization

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