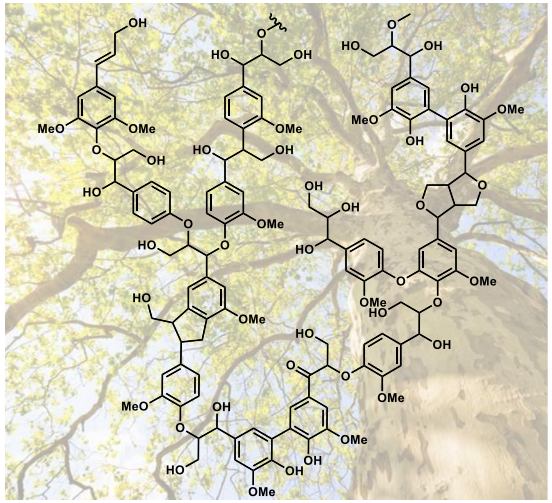
The Biosynthesis of Lignin

Abigail Halloran

10/15/26

Group Meeting



Lignin Biosynthesis

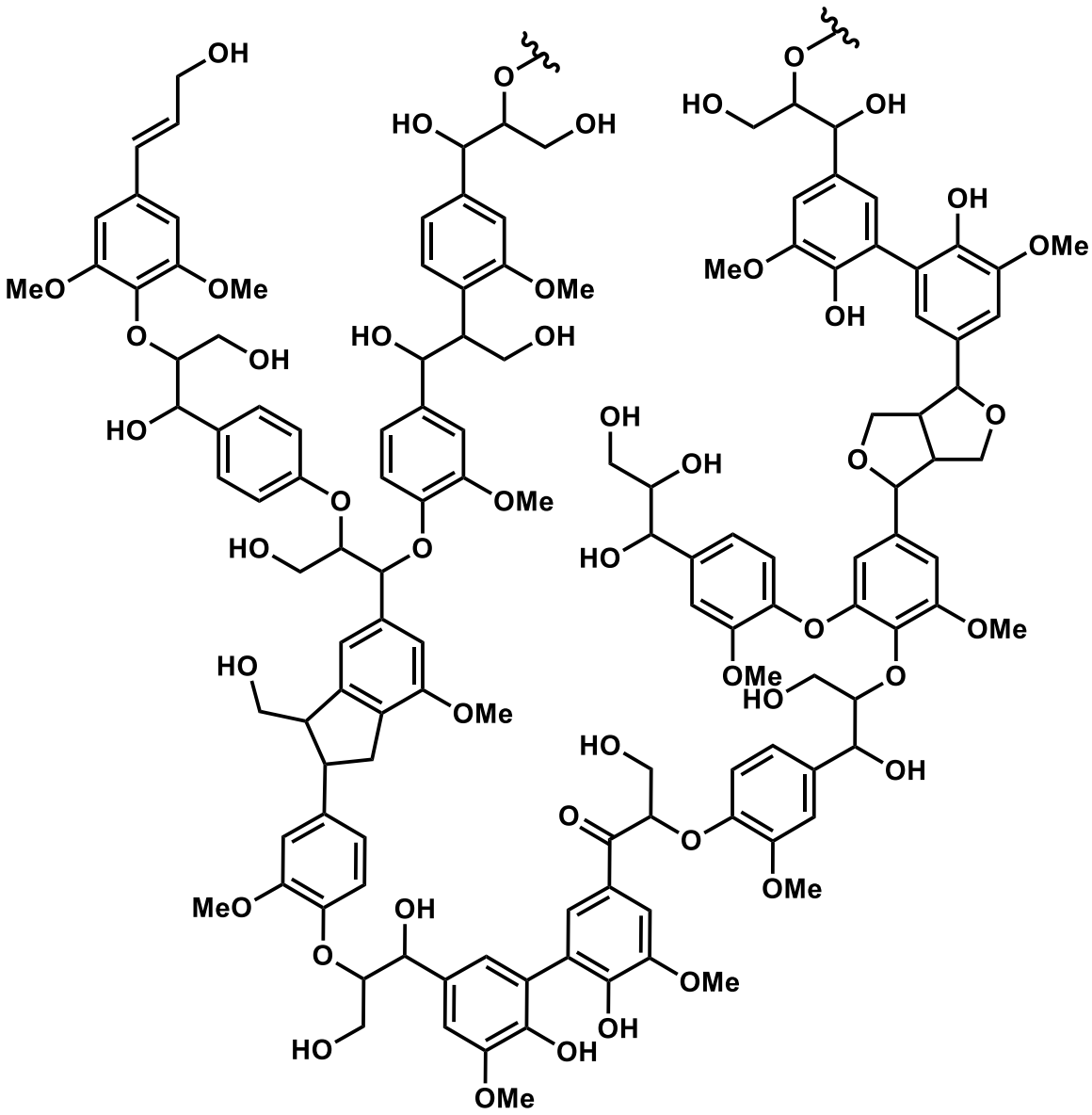
What is lignin?

Lignin is the most abundant natural aromatic polymer

Where does it come from?

It is one of the major cell-wall components of wood and grass species, along with cellulose





Plant Physiol. **2010**;153(3):895–905.

Lignin Biosynthesis

Lignin Applications

Lignin in the Paper Industry



Cellulose → Paper

Lignin → Burning for fuel

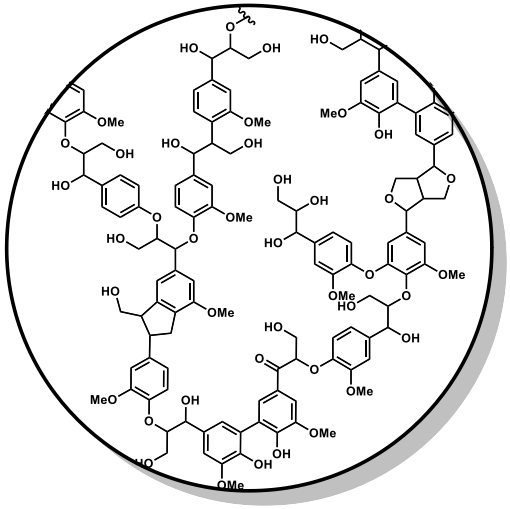
Lignin Beyond the Paper Industry



Carbon Fibers

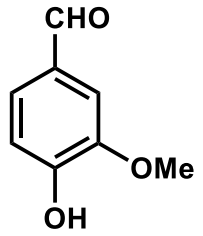


Adhesives and Glues





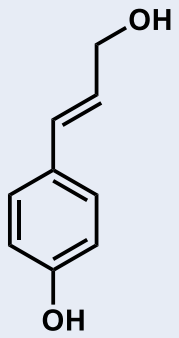
Paints and Coatings



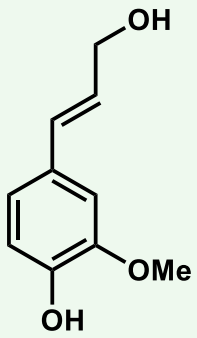
Vanillin

Lignin Chemical Structure

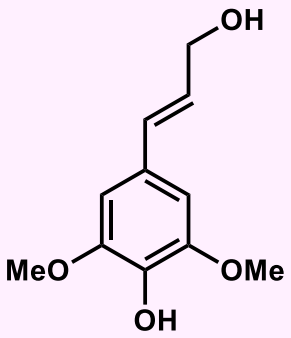
Lignin results from the oxidative coupling of 4-hydroxyphenylpropanoids



p-coumaryl alcohol
(H lignin)



Coniferyl alcohol
(G lignin)



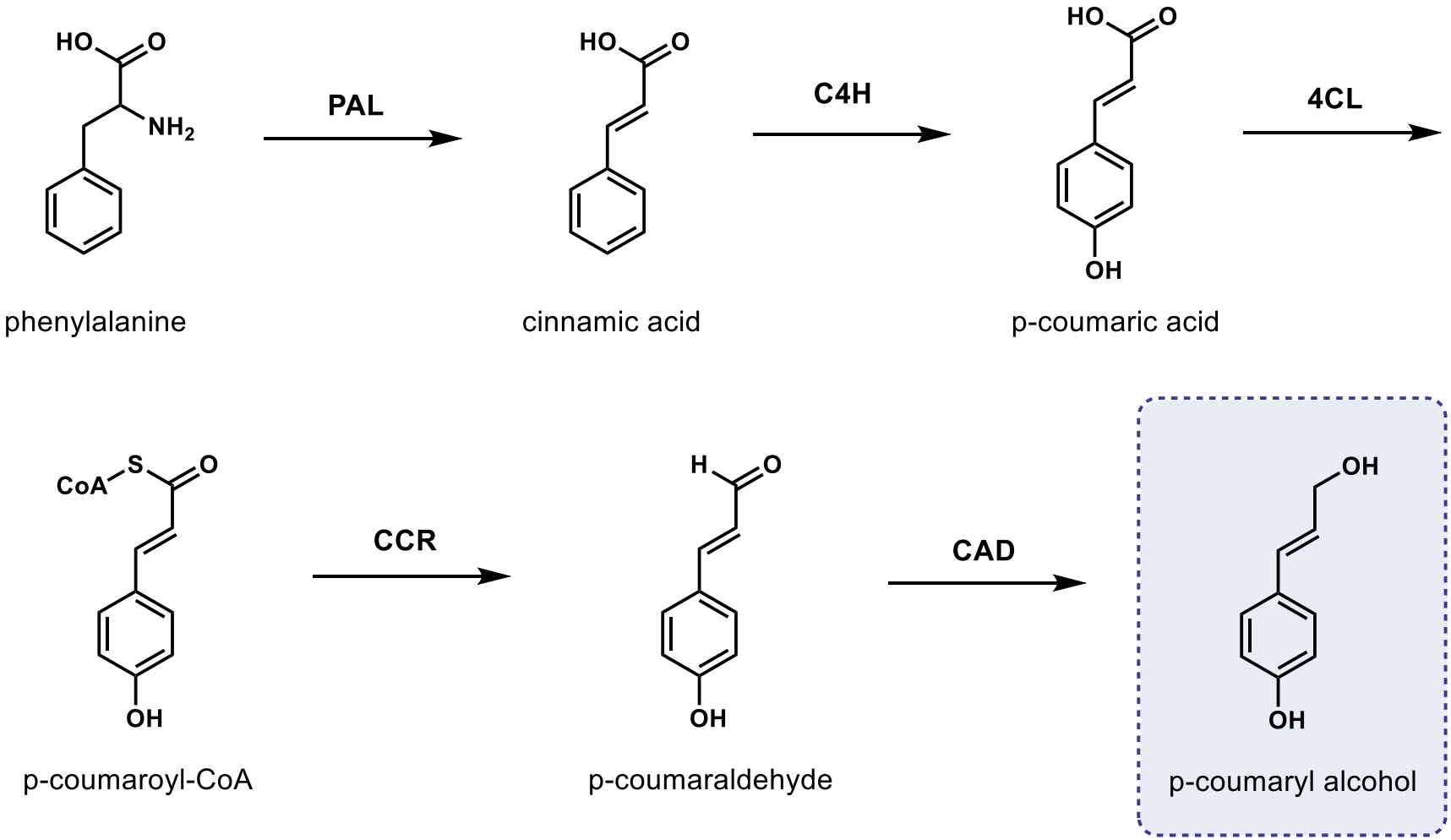
Sinapyl alcohol
(S lignin)

Lignin is made up of monomers derived from phenylalanine

Plant Physiol. **2010**;153(3):895–905.

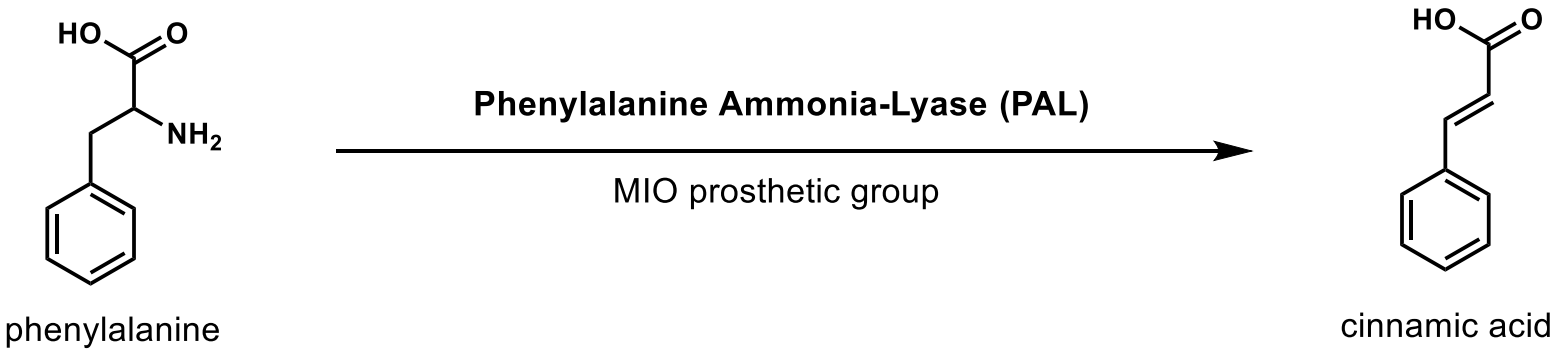
Lignin Biosynthesis

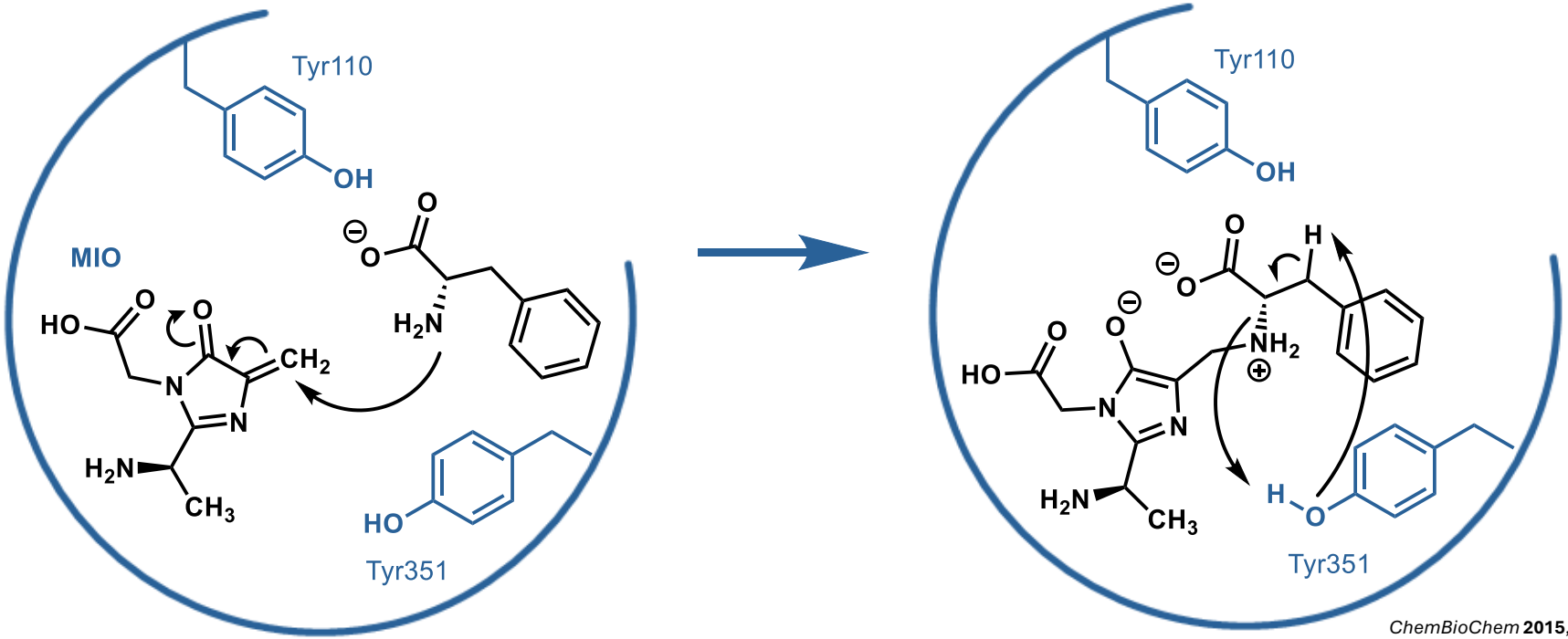
Pathway to p-coumaryl alcohol (H lignin)



Plant Physiol. **2010**;153(3):895–905.

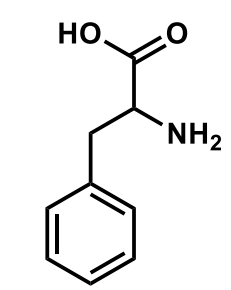
Pathway to p-coumaryl alcohol (H lignin)





ChemBioChem **2015**, *16*, 2283.

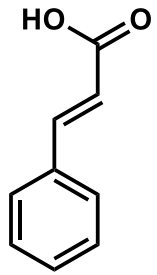
Pathway to p-coumaryl alcohol (H lignin)



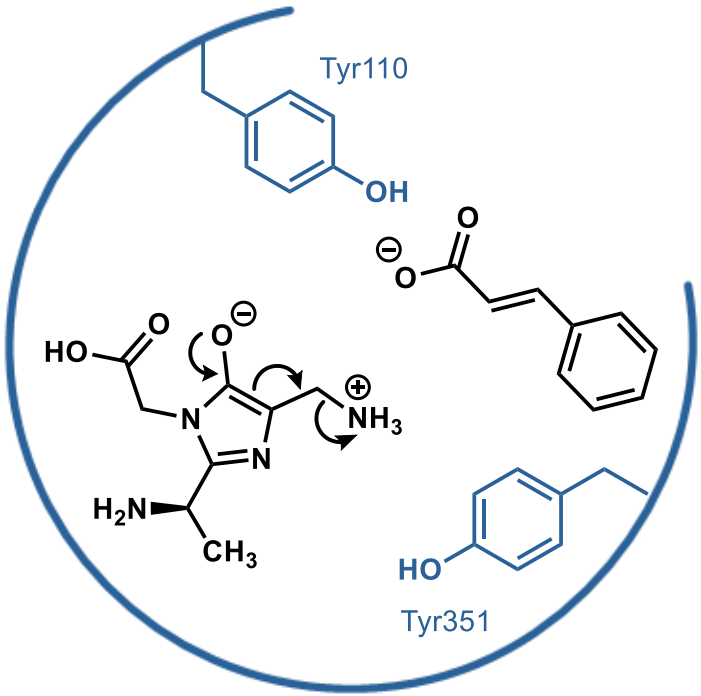
phenylalanine

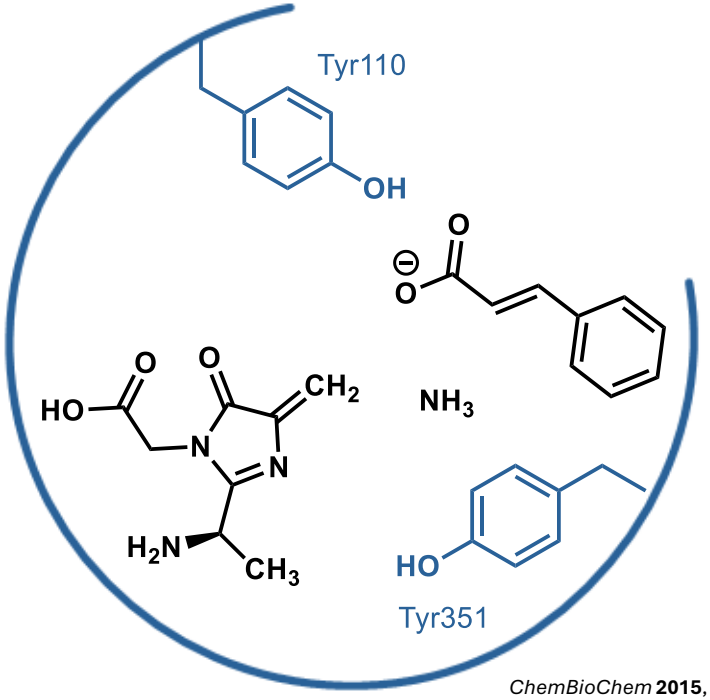
Phenylalanine Ammonia-Lyase (PAL)

MIO prosthetic group



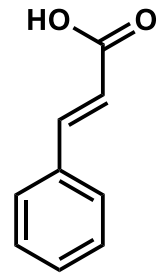
cinnamic acid





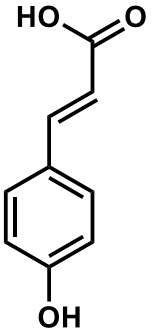
ChemBioChem **2015**, *16*, 2283.

Pathway to p-coumaryl alcohol (H lignin)

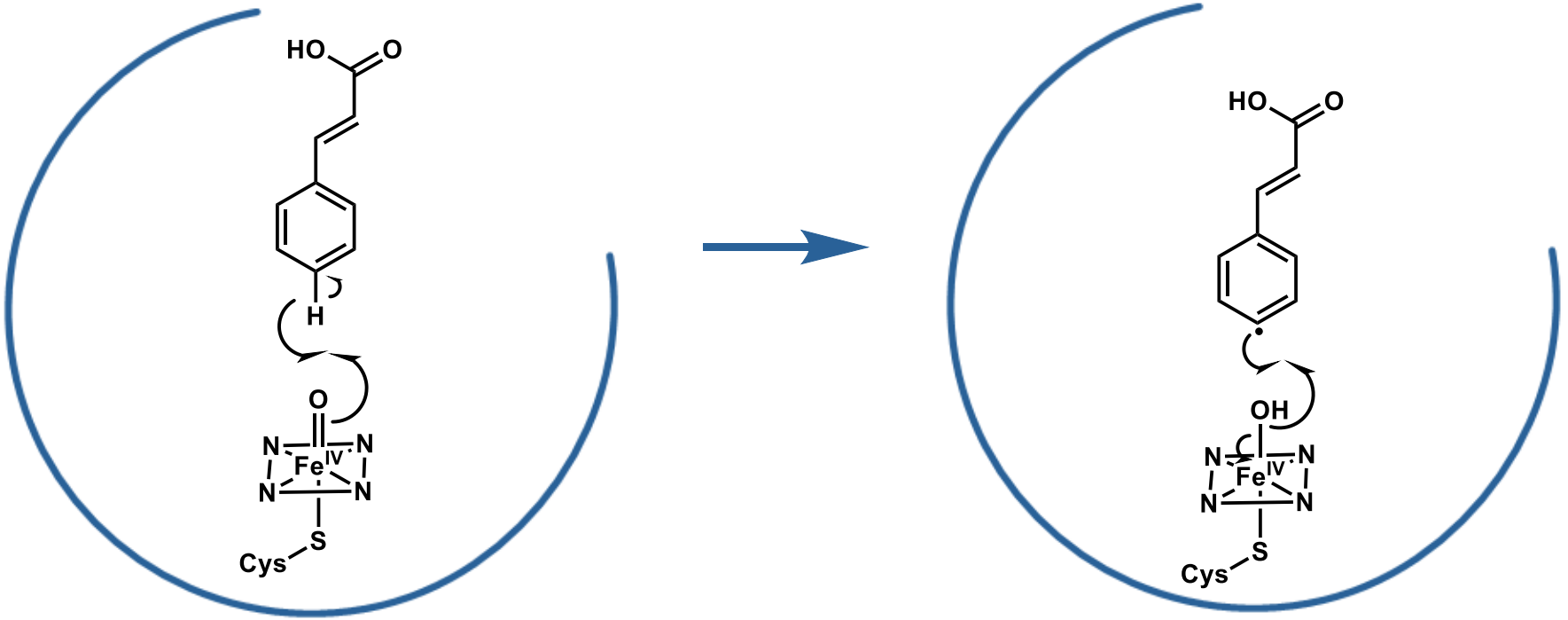


cinnamic acid

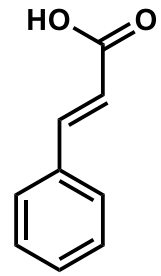
Cinnamate 4-hydroxylase (C4H)



p-coumaric acid

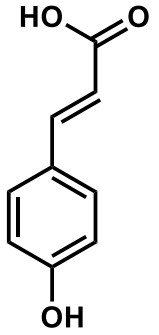


Pathway to p-coumaryl alcohol (H lignin)

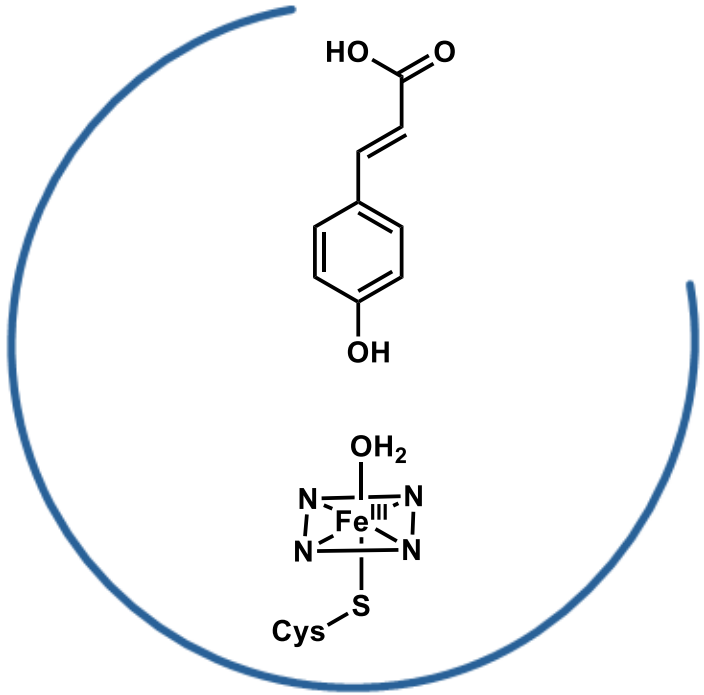


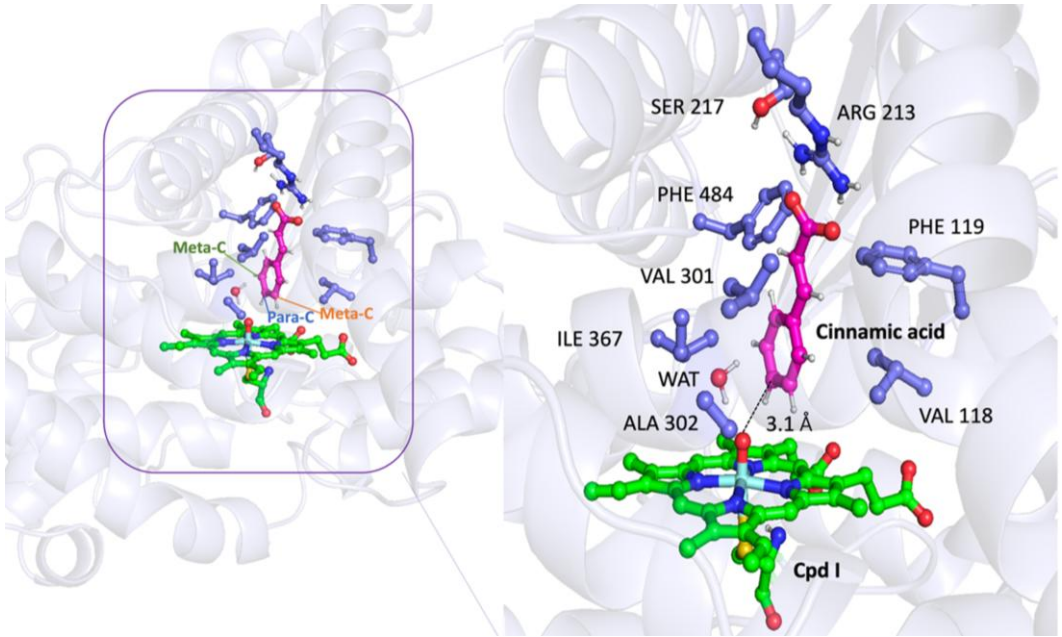
cinnamic acid

Cinnamate 4-hydroxylase (C4H)



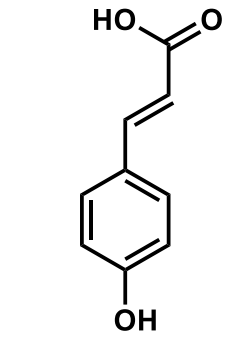
p-coumaric acid





Catal. Sci. Technol. (2025) 15 (23): 7067–7078.

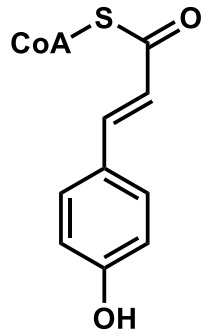
Pathway to p-coumaryl alcohol (H lignin)



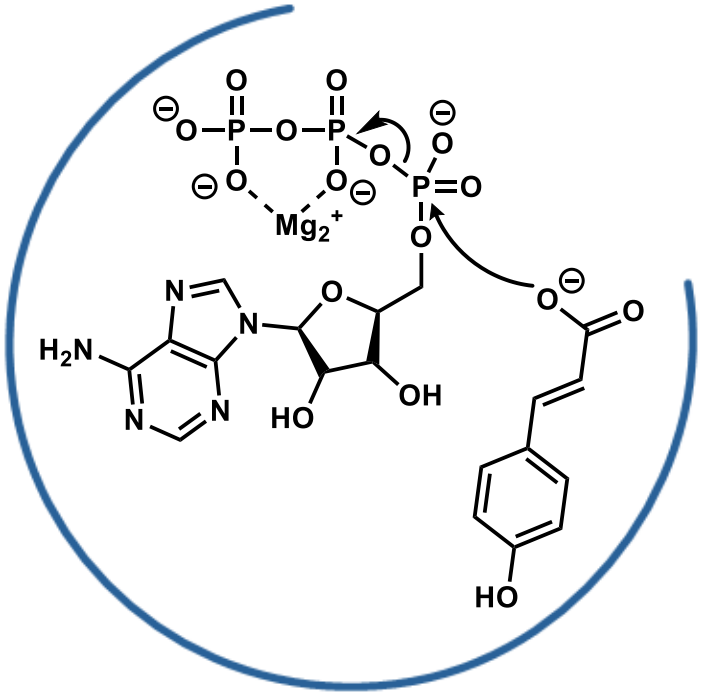
p-coumaric acid

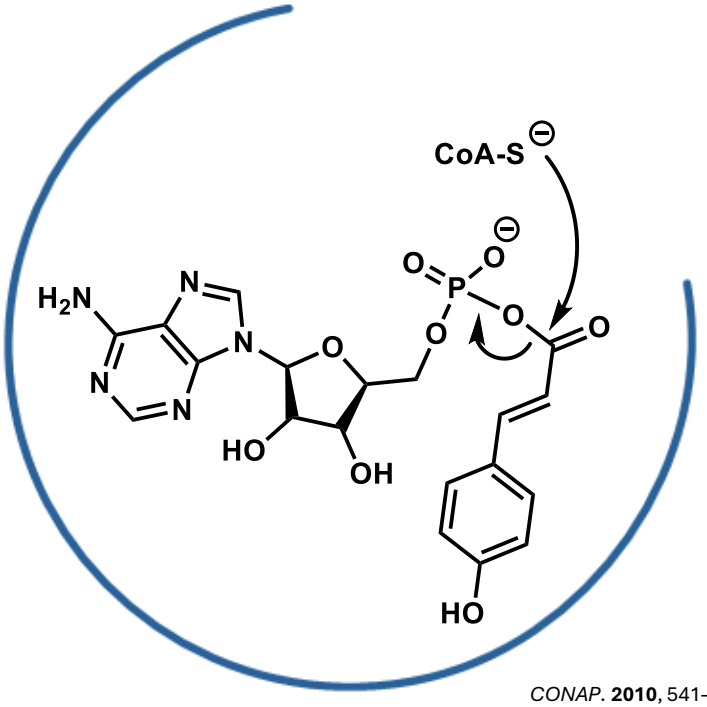
4-Coumarate:CoA ligase (4CL)

ATP + CoA → AMP + PPi



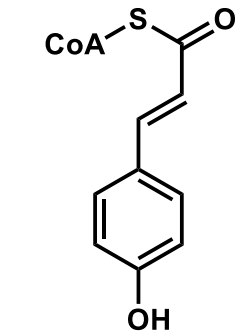
p-coumaroyl-CoA





Lignin Biosynthesis

Pathway to p-coumaryl alcohol (H lignin)

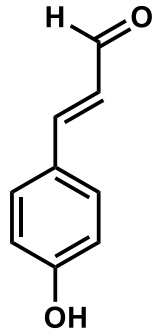


p-coumaroyl-CoA

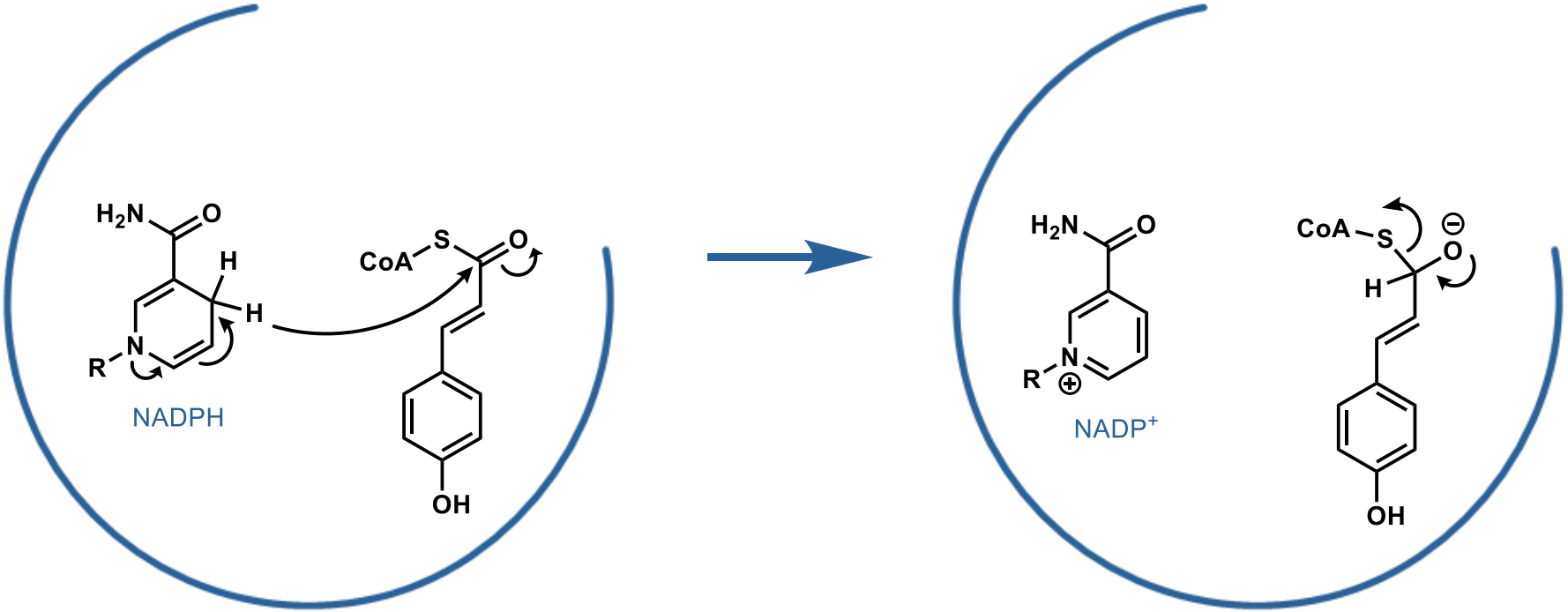
Cinnamoyl-CoA reductase (CCR)

NADPH

$NAD^+ + CoASH$

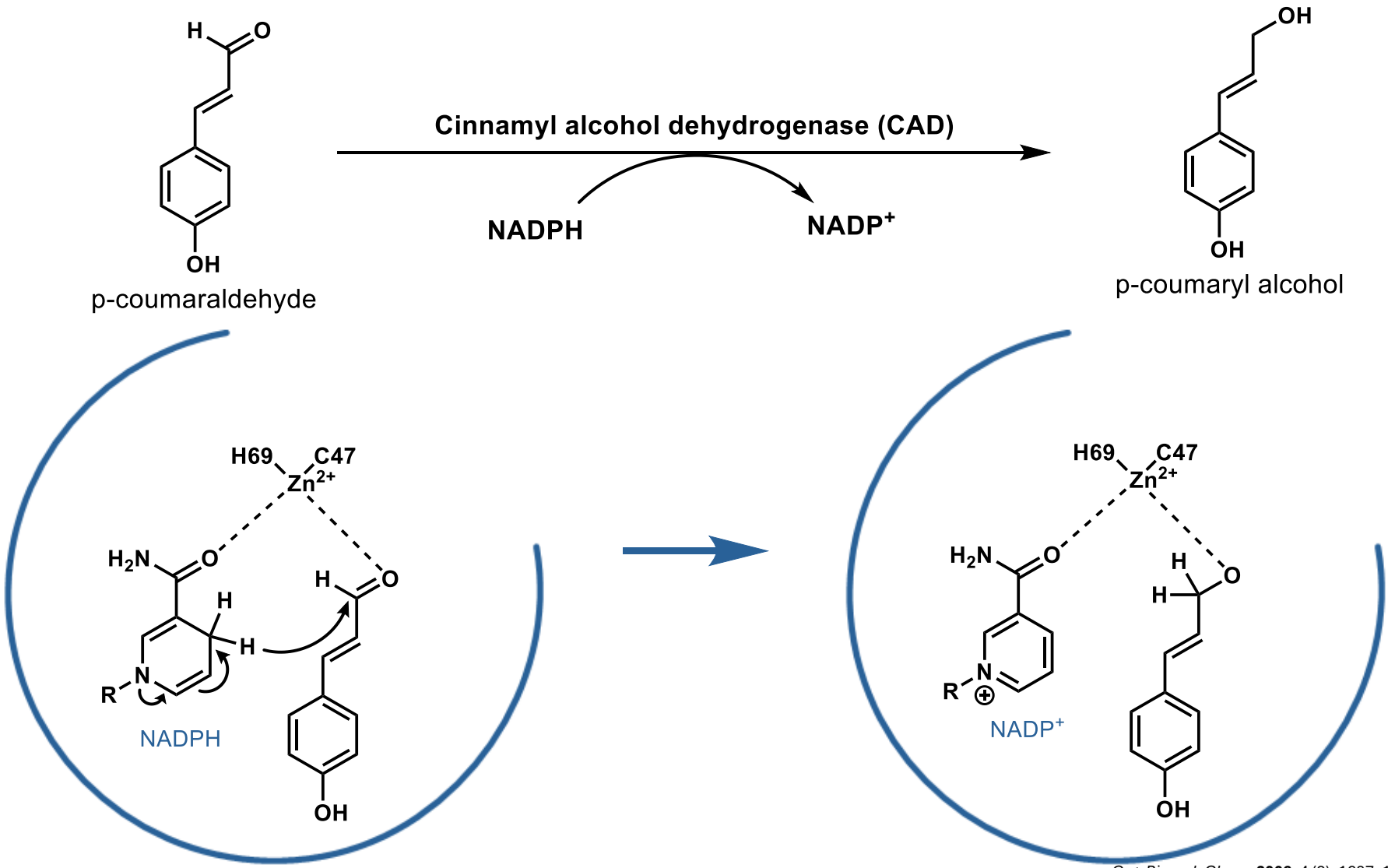


p-coumaraldehyde



Plant Physiol. **2016**;173(2):1031–1044.

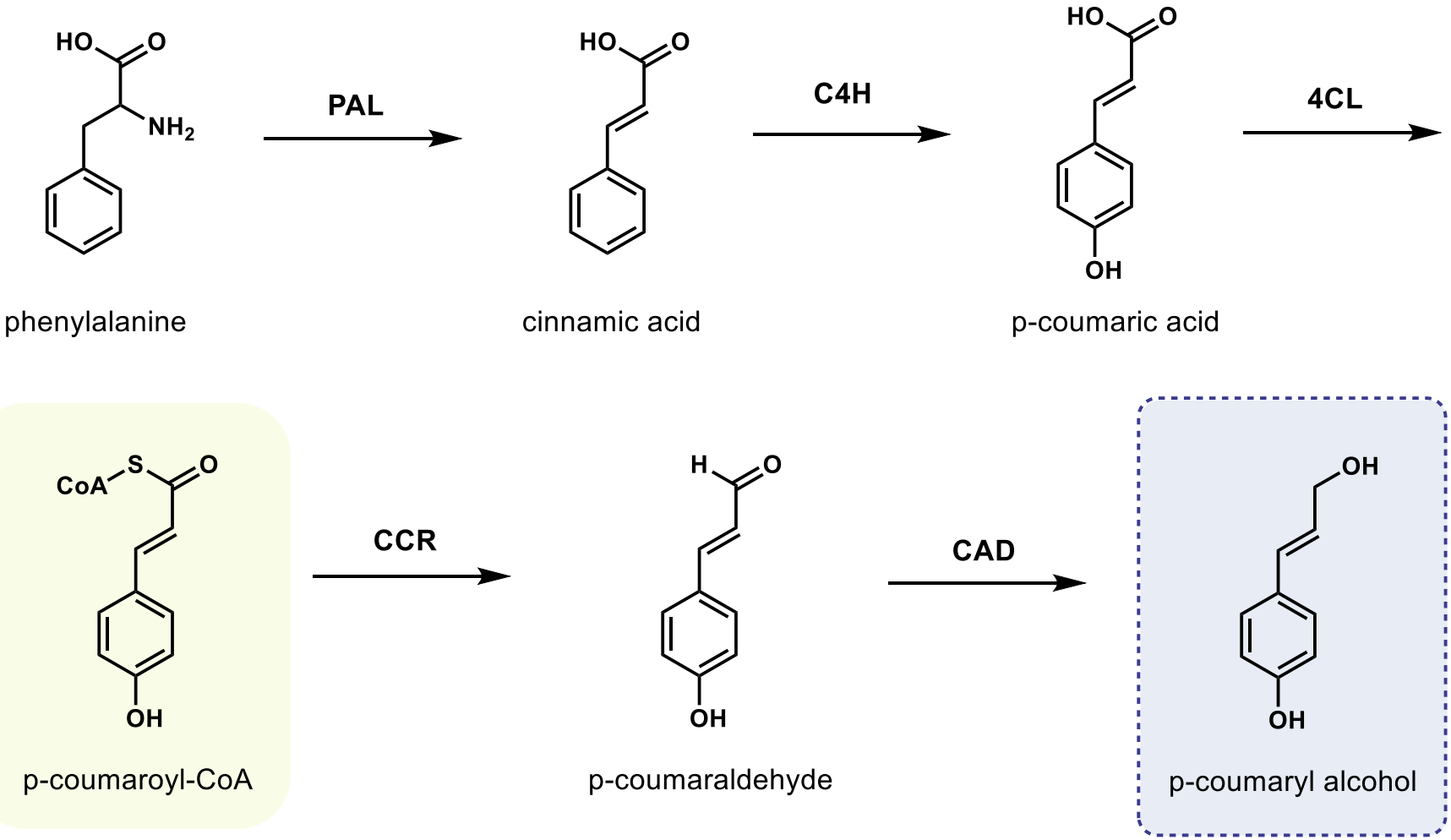
Pathway to p-coumaryl alcohol (H lignin)



Org. Biomol. Chem. **2006**. 4 (9): 1687–1697.

Lignin Biosynthesis

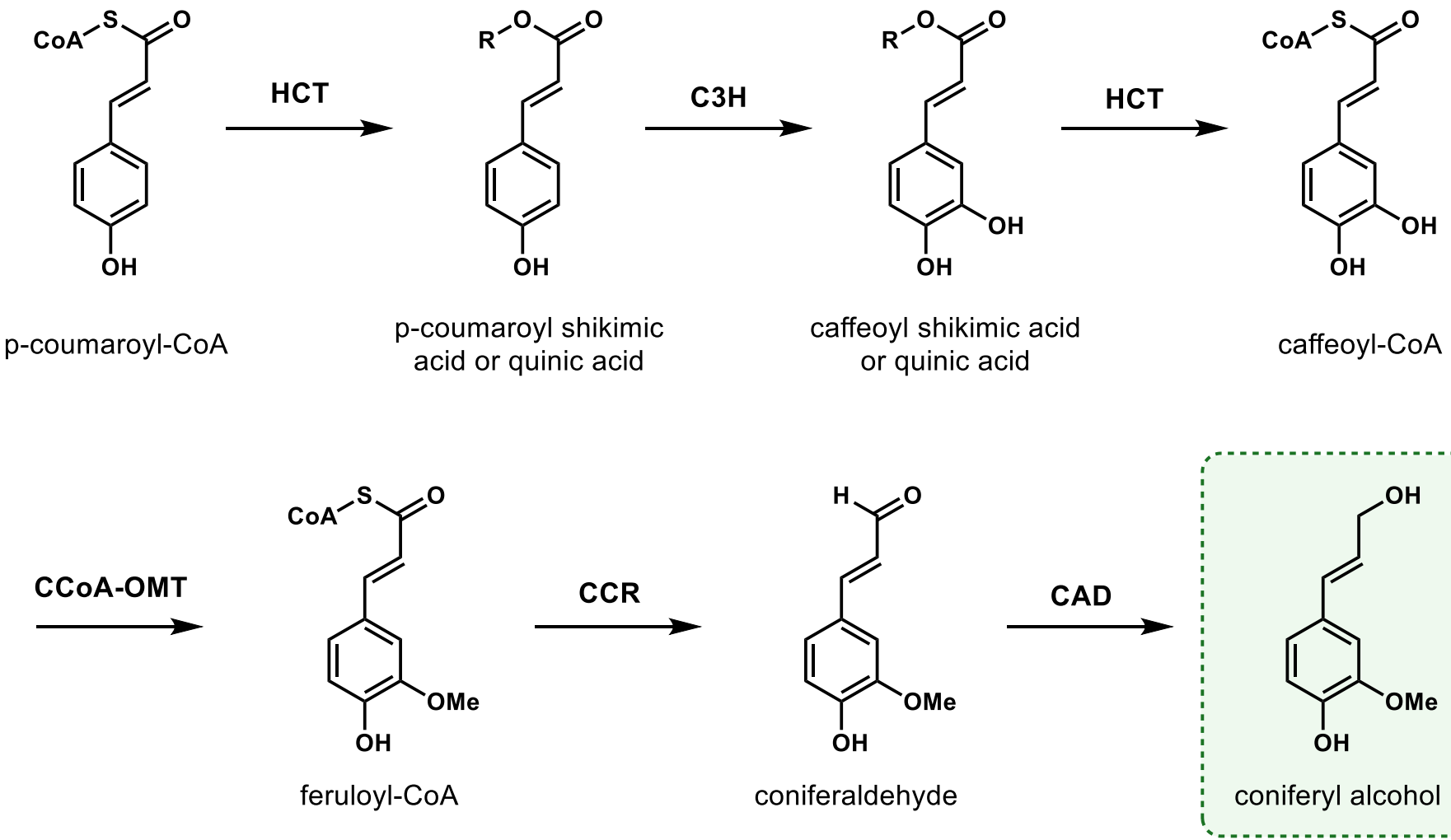
Pathway to p-coumaryl alcohol (H lignin)



Plant Physiol. **2010**;153(3):895–905.

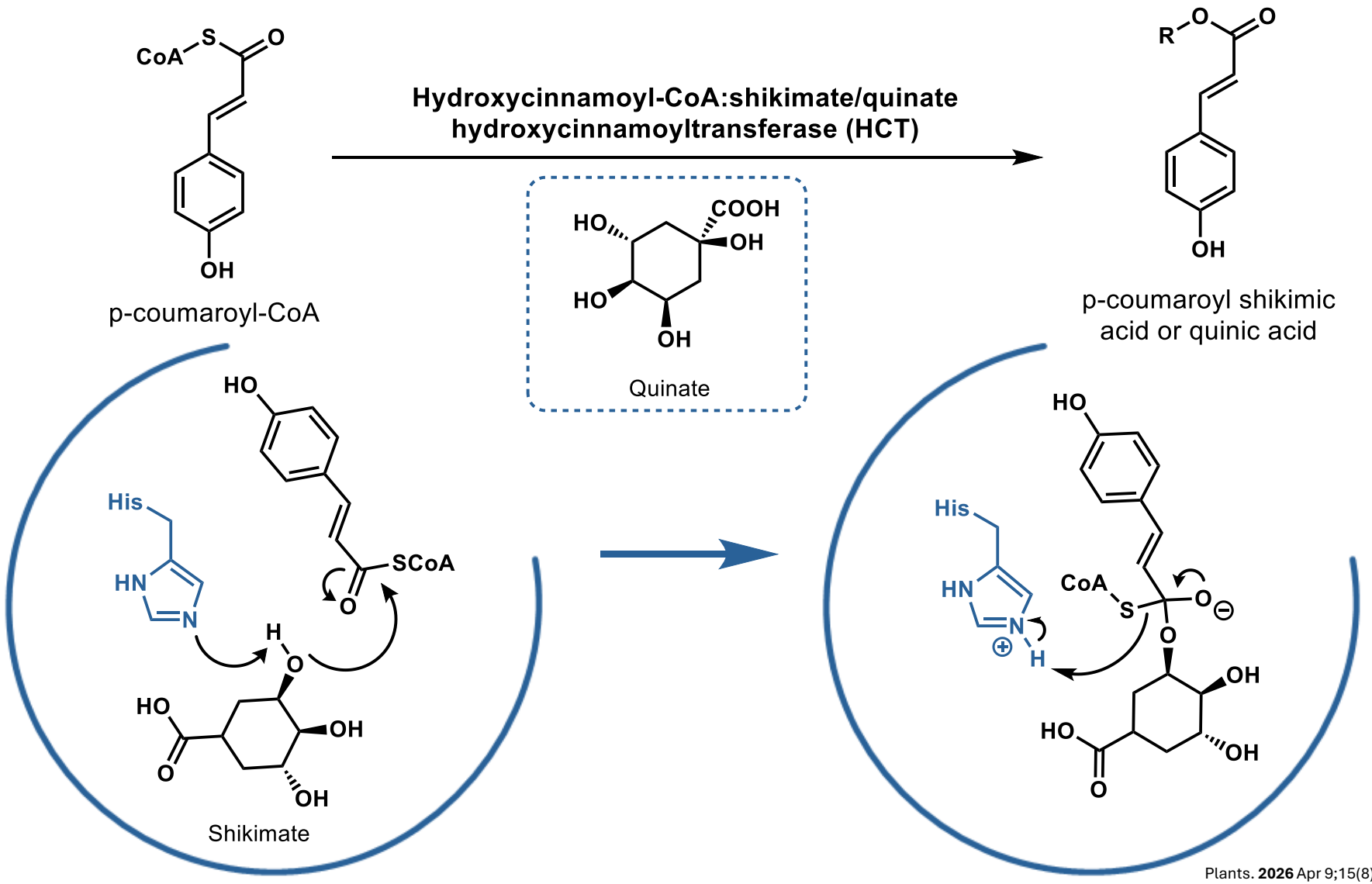
Lignin Biosynthesis

Pathway to coniferyl alcohol (G lignin)



Plant Physiol. **2010**;153(3):895–905.

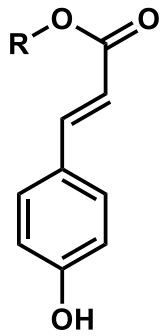
Pathway to coniferyl alcohol (G lignin)



Plants. **2026** Apr 9;15(8):1162.

Lignin Biosynthesis

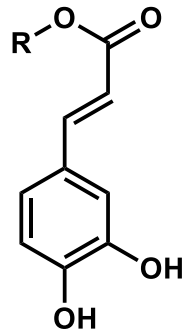
Pathway to coniferyl alcohol (G lignin)



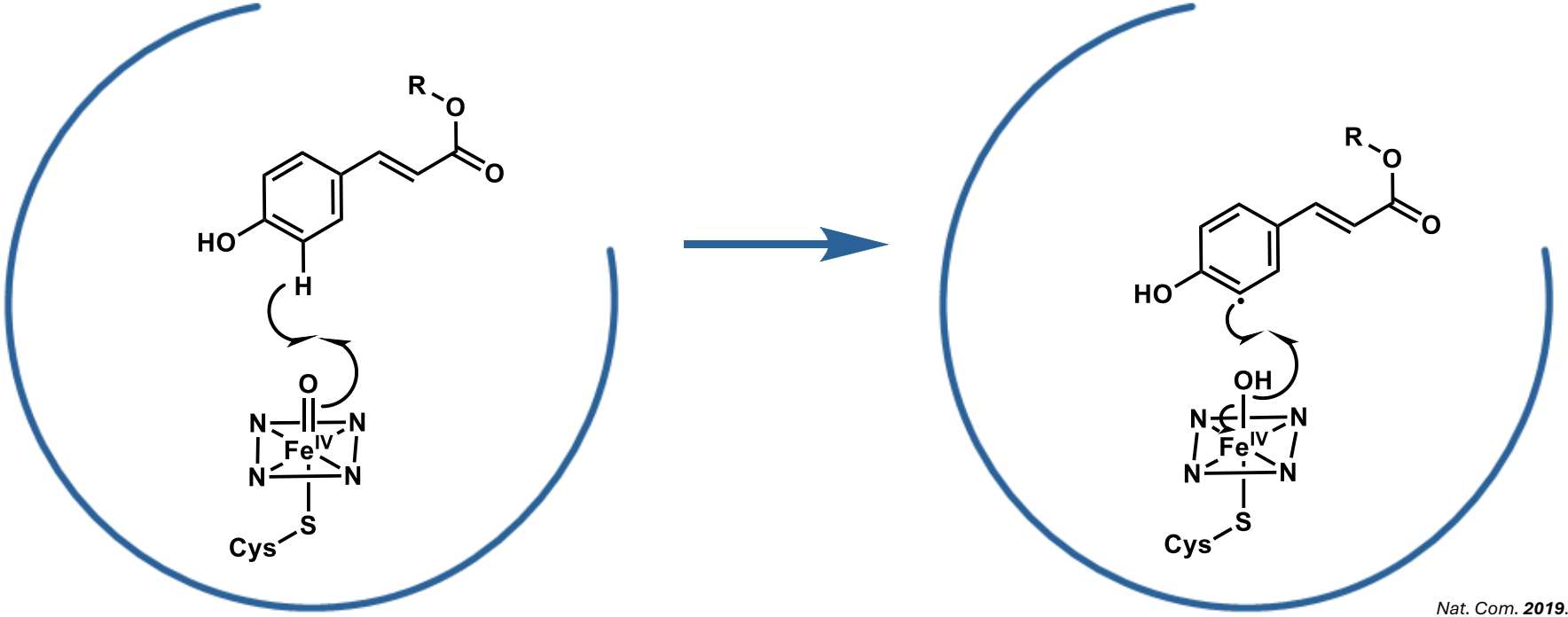
p-coumaroyl shikimic acid or quinic acid

p-Coumarate 3-hydroxylase (C3H)

*Similar cytochrome P450 Mechanism as C4H

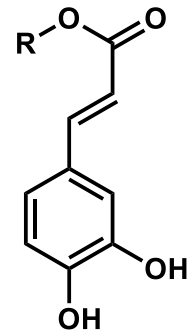


caffeoyl shimic or quinic acid



Nat. Com. ***2019***.1994.

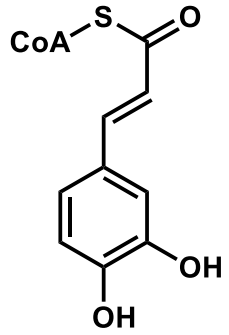
Pathway to coniferyl alcohol (G lignin)



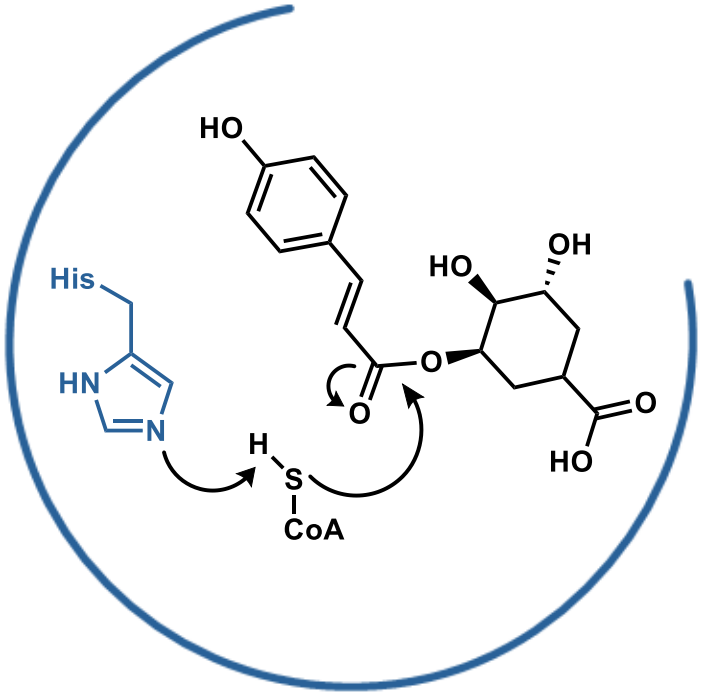
caffeoyl shimic or quinic acid

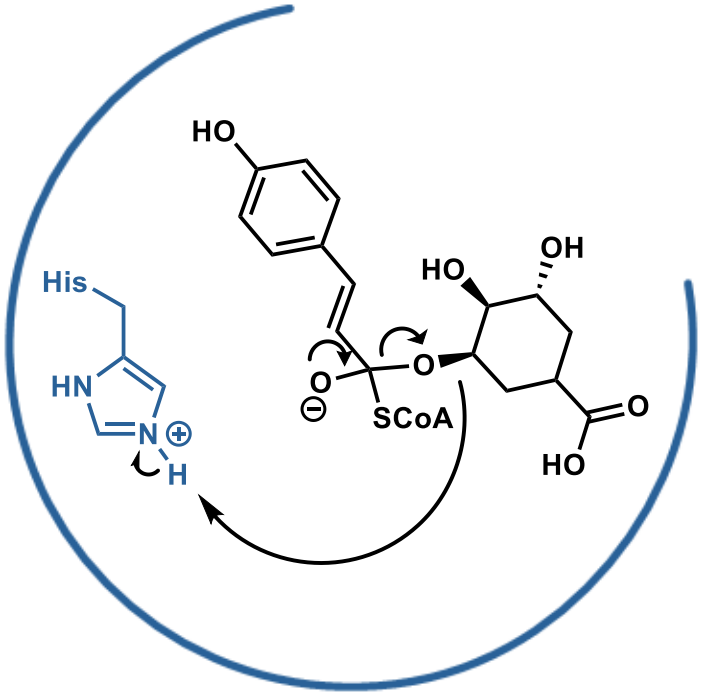
Hydroxycinnamoyl-CoA:shikimate/quinate hydroxycinnamoyltransferase (HCT)

*Same enzyme as previous step

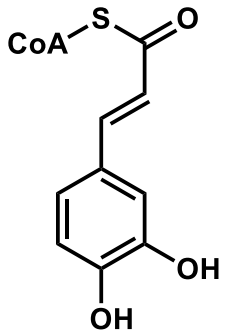


caffeoyl-CoA





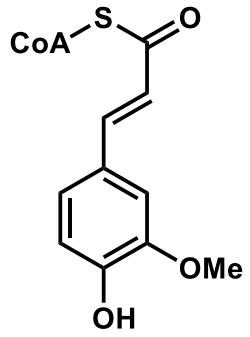
Pathway to coniferyl alcohol (G lignin)



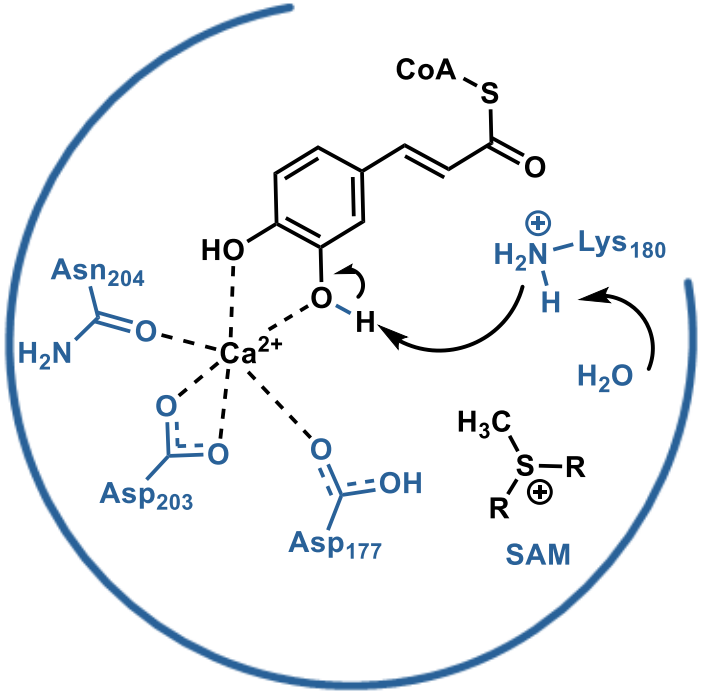
caffeoyl-CoA

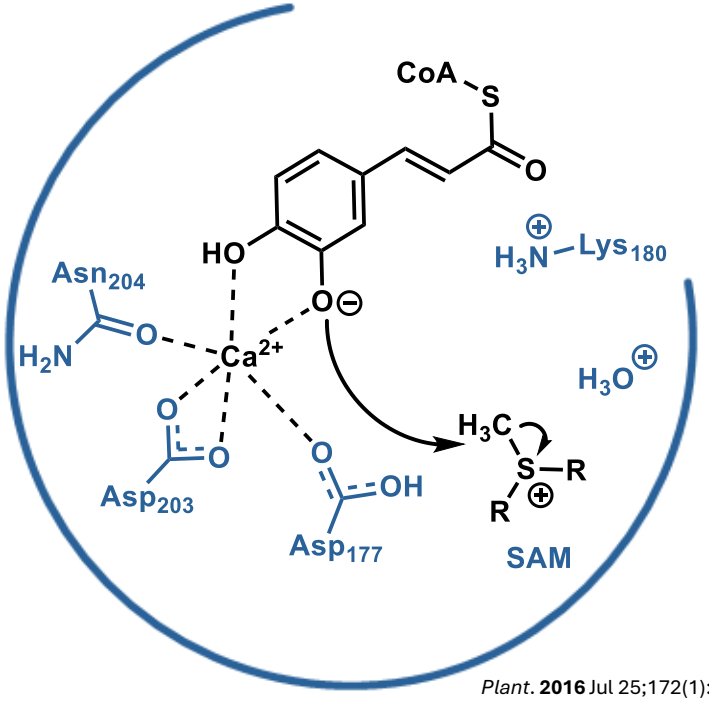
Caffeoyl-CoA O-methyltransferase (CCoA-OMT)

SAM-dependent methyltransferase



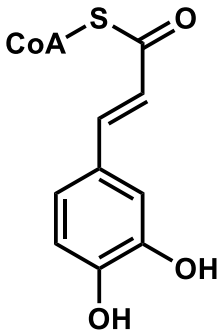
feruloyl-CoA





Plant. **2016** Jul 25;172(1):78–92

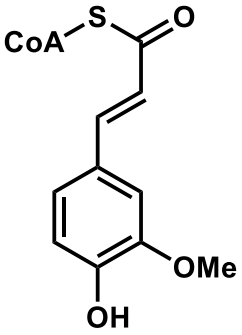
Pathway to coniferyl alcohol (G lignin)



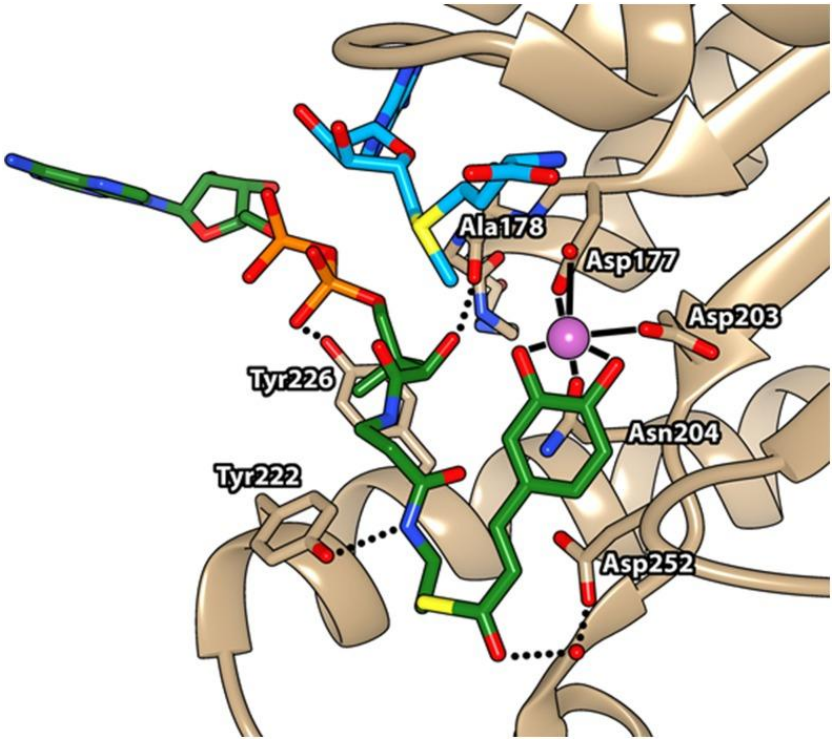
caffeoyl-CoA

Caffeoyl-CoA O-methyltransferase (CCoA-OMT)

SAM-dependent methyltransferase

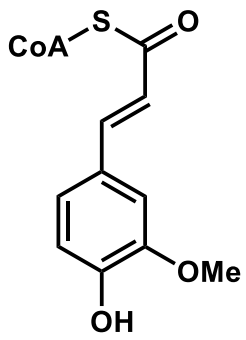


feruloyl-CoA



Lignin Biosynthesis

Pathway to coniferyl alcohol (G lignin)

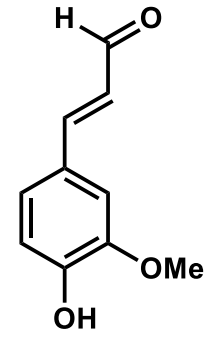


feruloyl-CoA

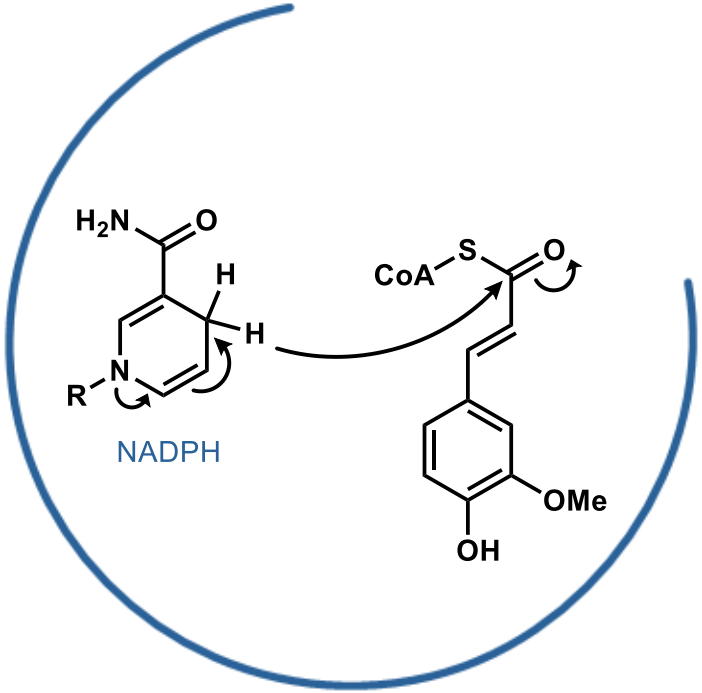
Cinnamoyl-CoA reductase (CCR)

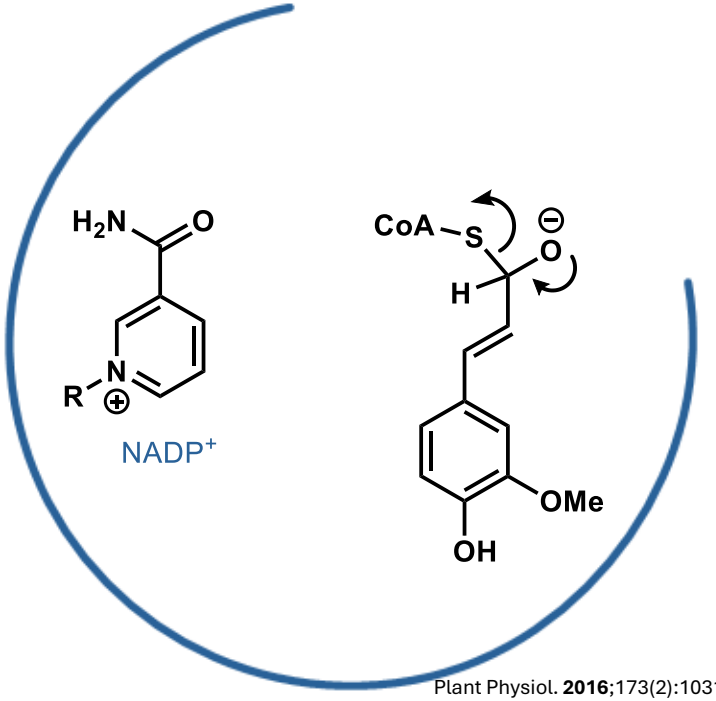
NADPH

$NAD^+ + CoASH$



coniferaldehyde

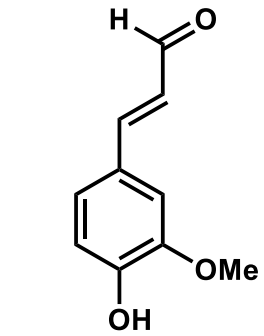




Plant Physiol. **2016**;173(2):1031–1044.

Lignin Biosynthesis

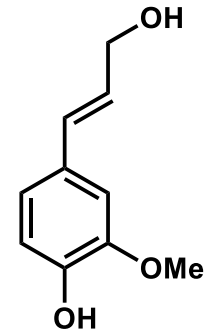
Pathway to coniferyl alcohol (G lignin)



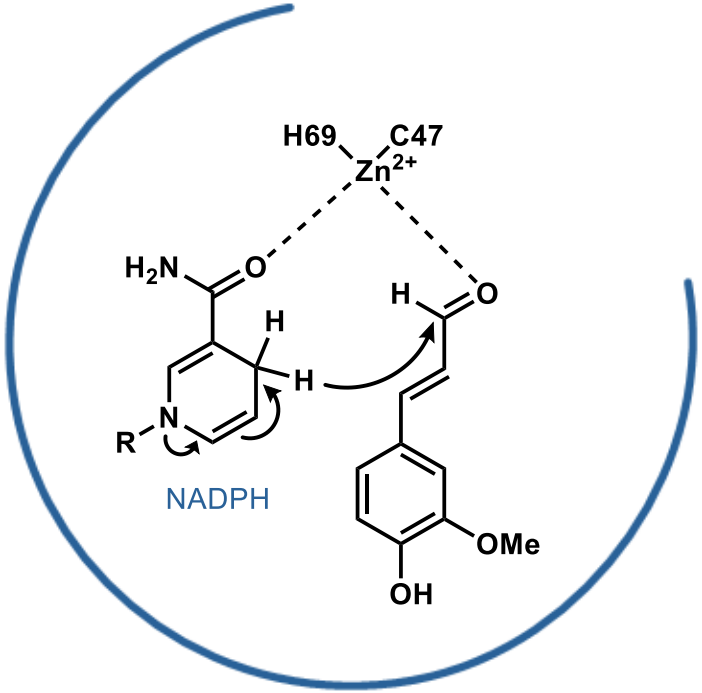
coniferaldehyde

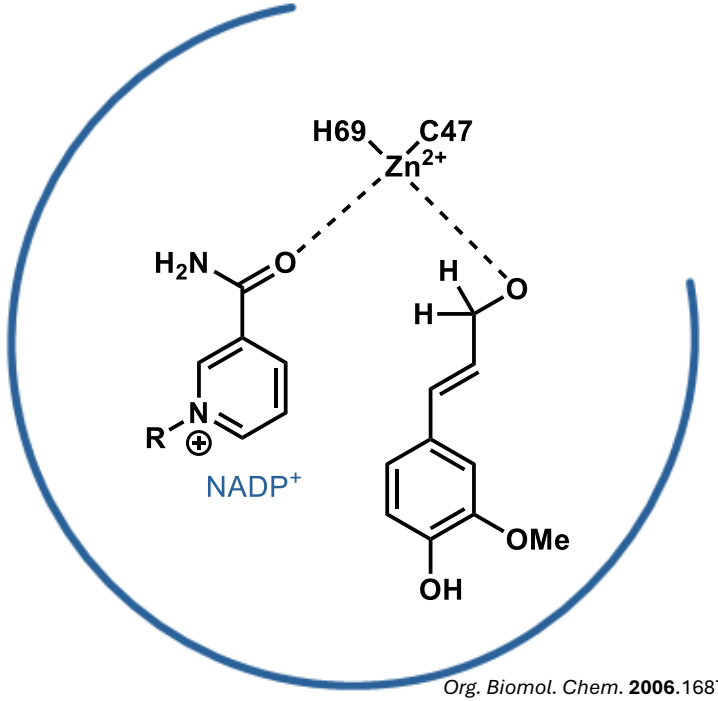
Cinnamyl alcohol dehydrogenase (CAD)

NADPH → $NADP^+$



coniferyl alcohol

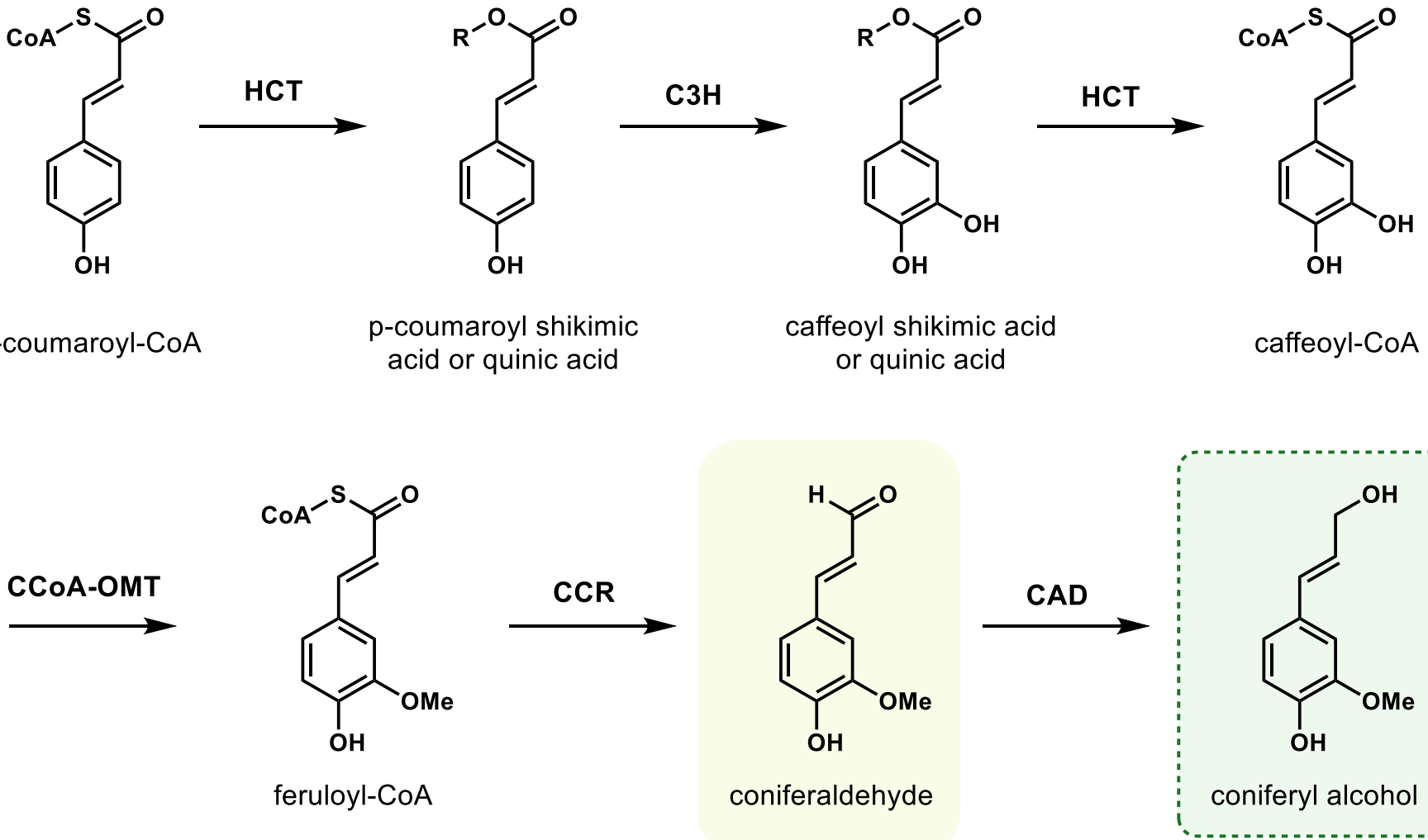




Org. Biomol. Chem. **2006**.1687–1697.

Lignin Biosynthesis

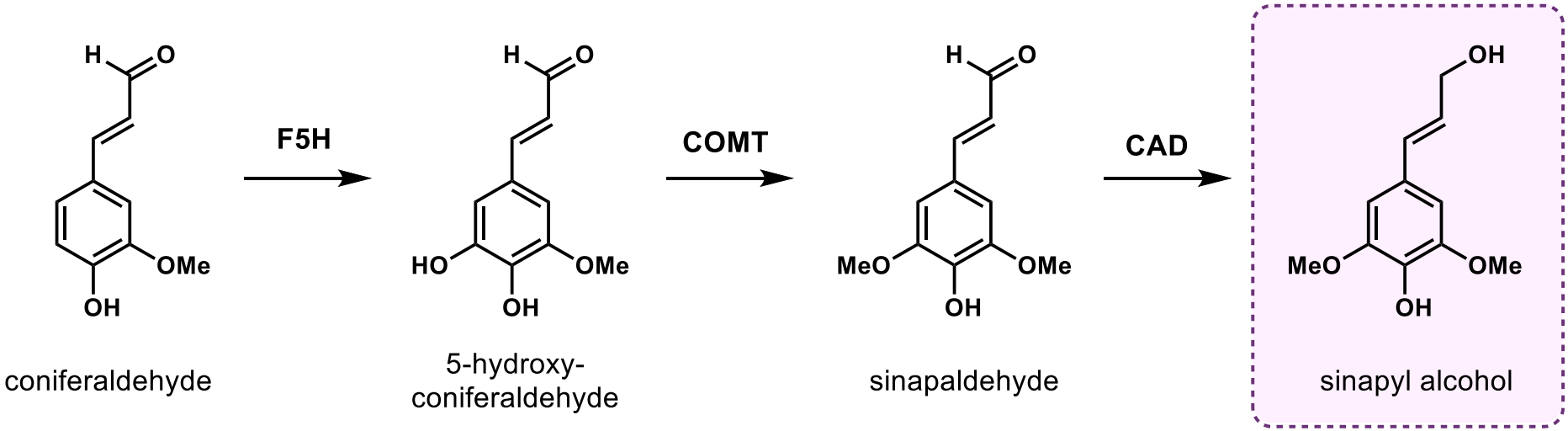
Pathway to coniferyl alcohol (G lignin)



Plant Physiol. **2010**;153(3):895–905.

Lignin Biosynthesis

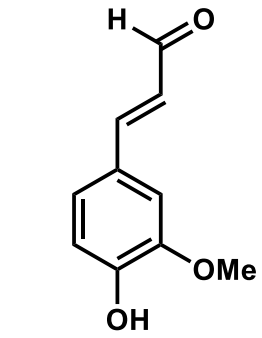
Pathway to sinapyl alcohol (S lignin)



Plant Physiol. **2010**;153(3):895–905.

Lignin Biosynthesis

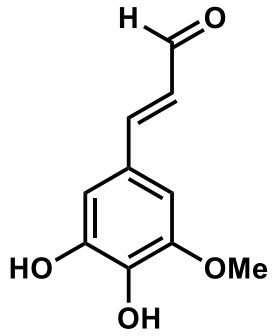
Pathway to sinapyl alcohol (S lignin)



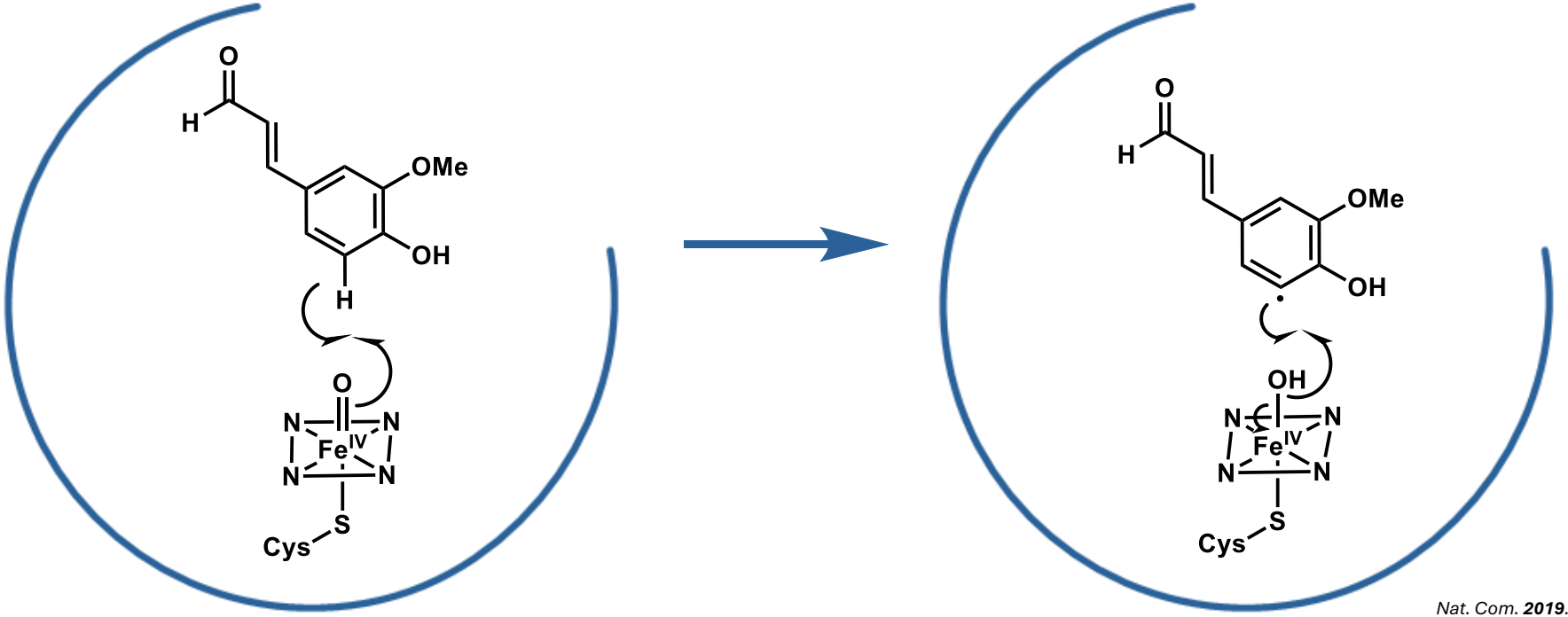
coniferaldehyde

Ferulate 5-hydroxylase (F5H)

Cytochrome p450

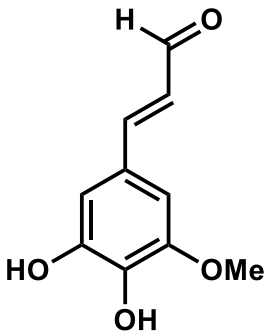


5-hydroxyconiferaldehyde



Nat. Com. ***2019***.1994.

Pathway to sinapyl alcohol (S lignin)

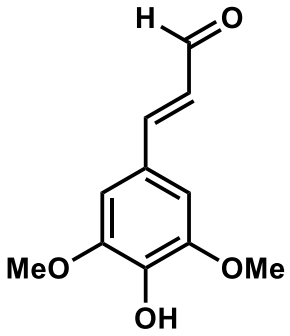


5-hydroxyconiferaldehyde

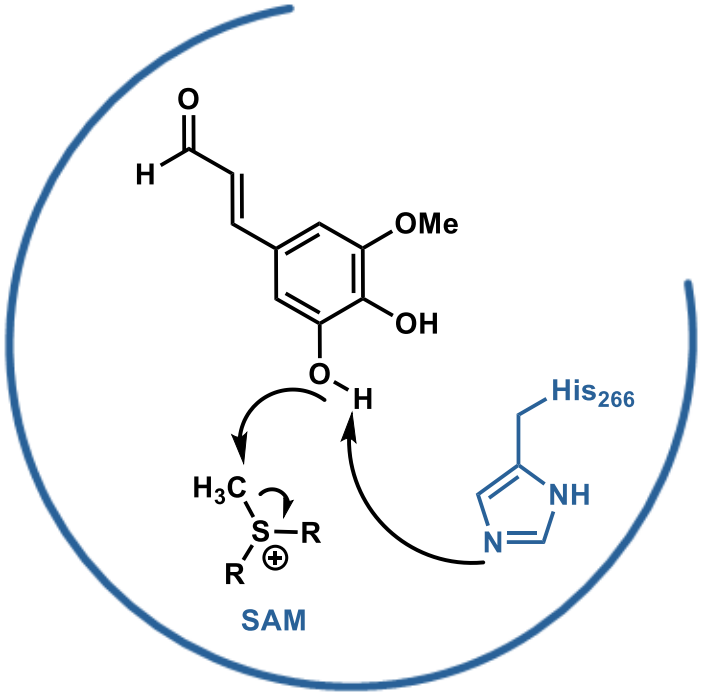
Caffeic acid O-methyltransferase (COMT)

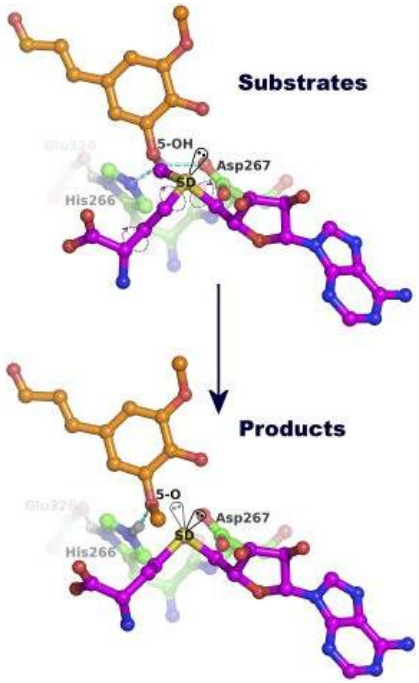
SAM dependent methyltransferase

*not calcium dependent like previous methyltransferase



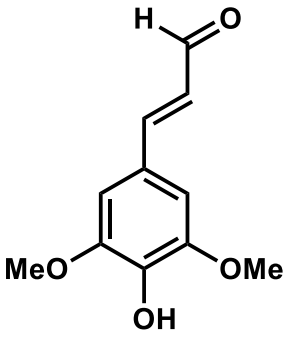
sinapaldehyde





Lignin Biosynthesis

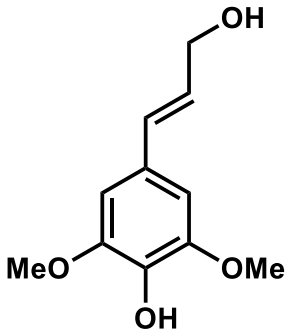
Pathway to sinapyl alcohol (S lignin)



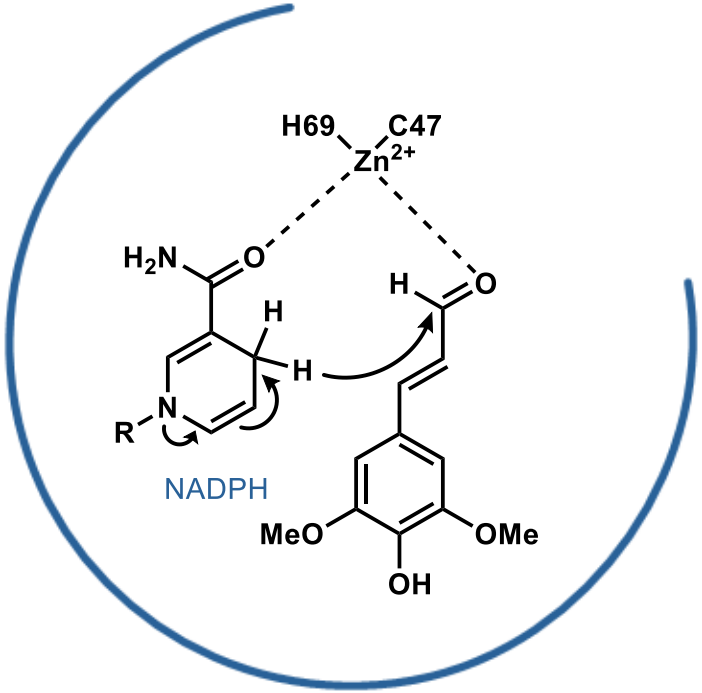
sinapaldehyde

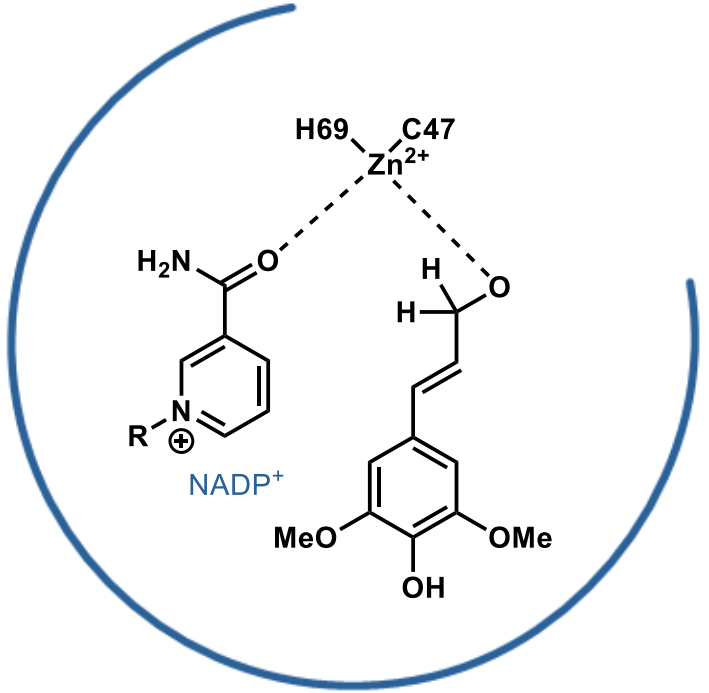
Cinnamyl alcohol dehydrogenase (CAD)

NADPH → $NADP^+$



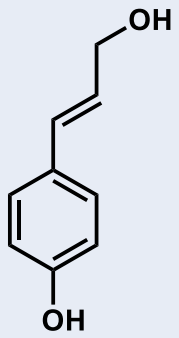
sinapyl alcohol



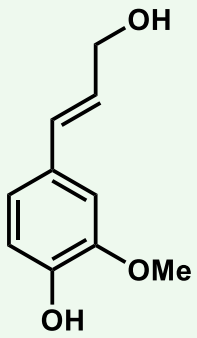


Lignin Chemical Structure

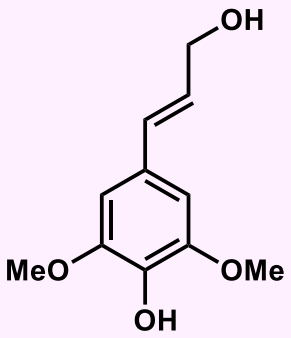
Lignin results from the oxidative coupling of 4-hydroxyphenylpropanoids



p-coumaryl alcohol
(H lignin)



Coniferyl alcohol
(G lignin)



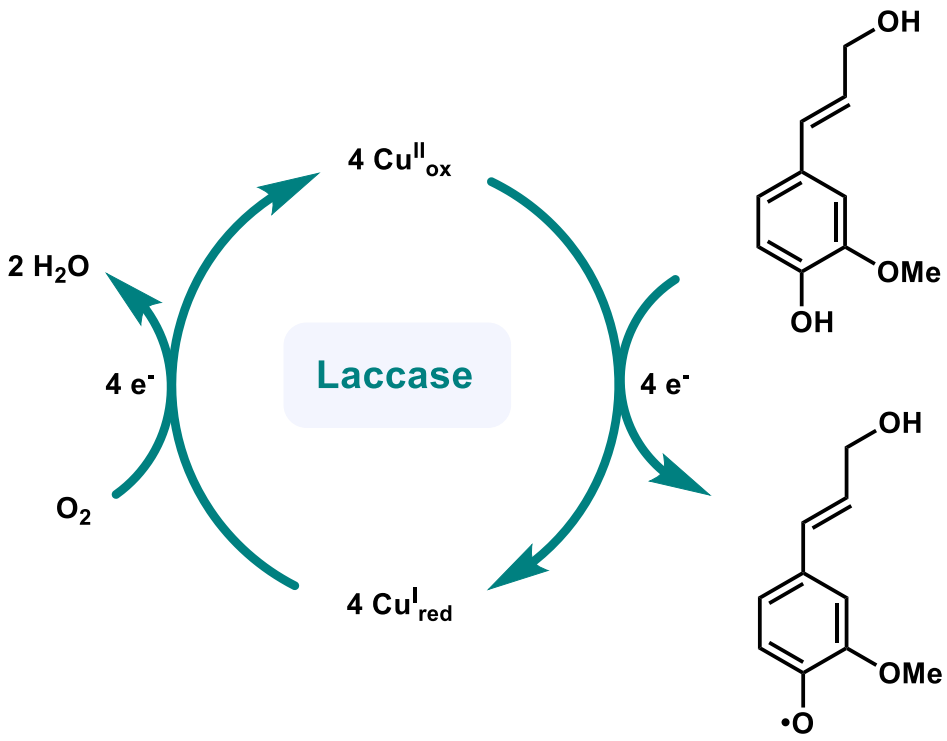
Sinapyl alcohol
(S lignin)

Lignin is made up of monomers derived from phenylalanine

Plant Physiol. **2010**;153(3):895–905.

Lignin Polymerization

Lignin formation is biologically controlled by laccases and peroxidases

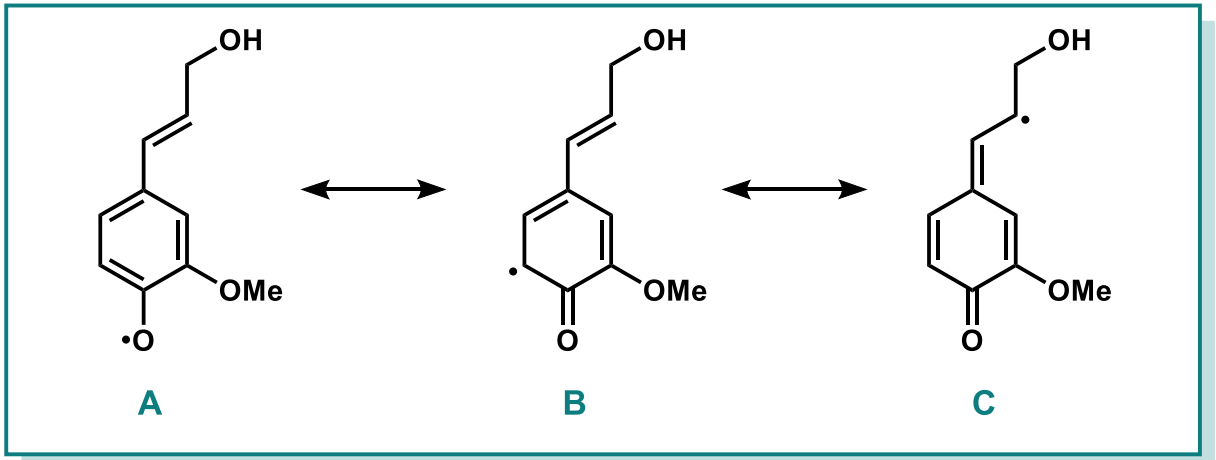


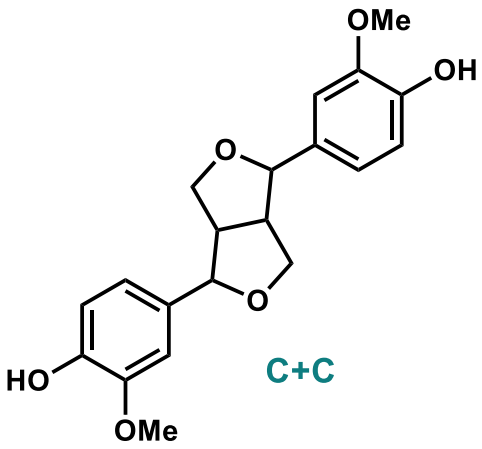
It is still unclear whether the final composition of lignin is determined by monomer availability, laccase/peroxidase specificity, or both

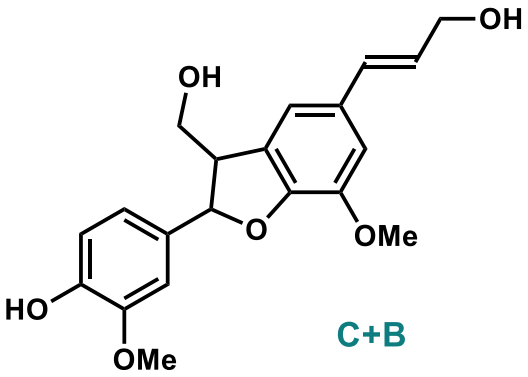
Plant Physiol. **2010**;153(3):895–905.

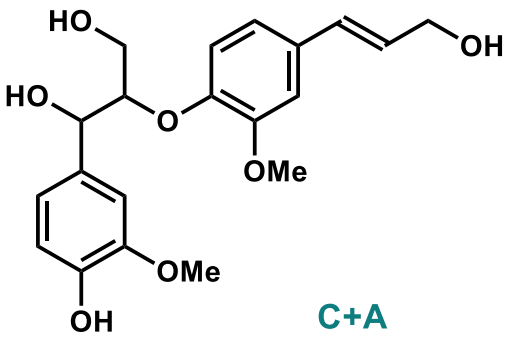
Lignin Biosynthesis

Lignin Polymerization - chain growth polymerization









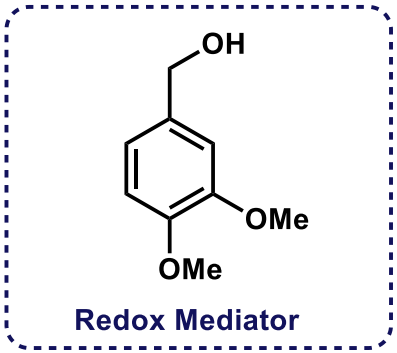
Possibilities from the dimerization of coniferyl alcohol

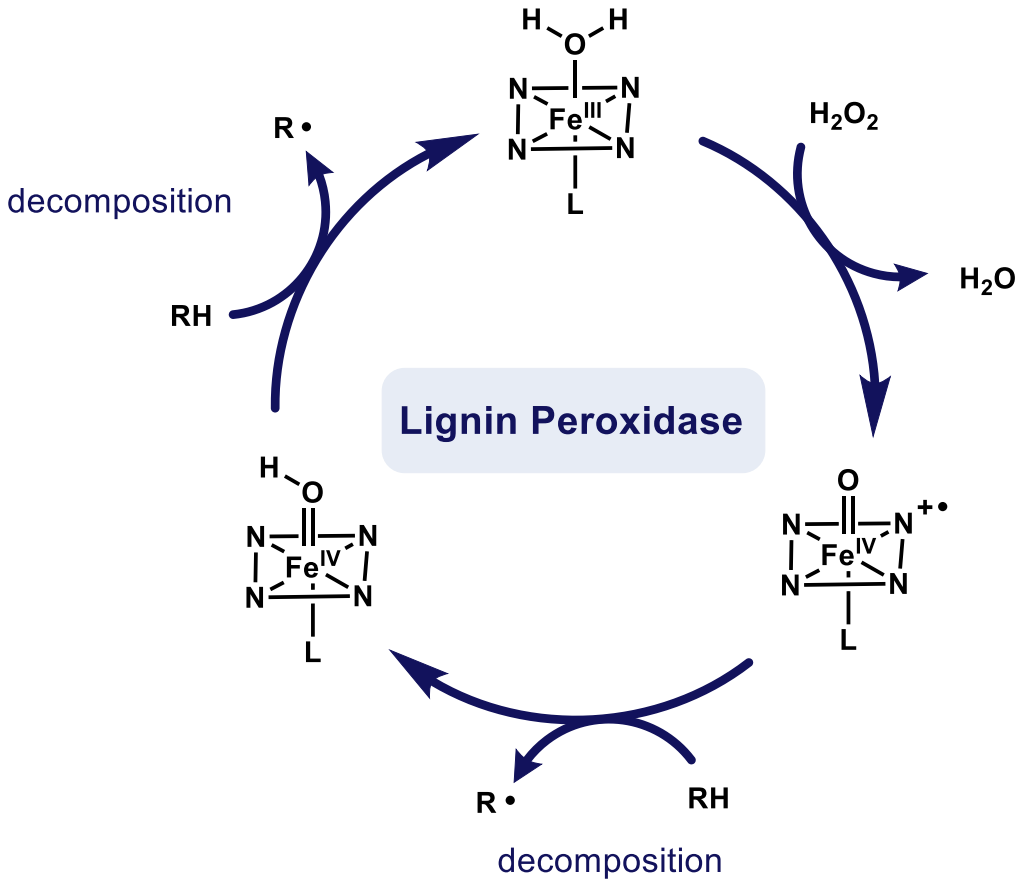
Plant Physiol. **2010**;153(3):895–905.

Lignin Depolymerization

In nature, white-rot fungi are the most effective natural lignin degraders. They release extracellular enzymes, including lignin peroxidase, manganese peroxidase, versatile peroxidase, and laccase, to break down lignin.







PNAS. **118**, e2017381118 (2021).