

Wood Chemistry

Wood Chemistry

PSE 406/Chem E 470

Lecture 9

Lignin Biosynthesis

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Class Agenda

Lignin I

- Basic Lignin Biosynthesis
- Nomenclature
- Methoxyl Groups
- Phenoxy Radical Formation
- Radical Coupling

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Random Lignin Information

- Anselme Payen 1838: Reacts wood with nitric acid and then sodium hydroxide. Undissolved material he names cellulose.
- Schulze 1857: Names dissolved material lignin from the Latin lignum meaning wood.
- Phenolic Polymer - The Glue that Holds the Fibers Together
- Polydisperse (Large and Small Polymers)
- 3 Dimensional Networks - Branched Polymer

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Lignin Biosynthesis I

CO₂ → [] → Glucose → Shikimate Pathway

Photosynthetic Pathways

Notes

L-Tyrosine L-Phenylalanine Shikimic Acid

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Lignin Biosynthesis II

L-Tyrosine → Cinnamate Pathway → L-Phenylalanine

p-Coumaryl Alcohol Coniferyl Alcohol Sinapyl Alcohol

Notes

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Lignin Biosynthesis Nomenclature

γ C — Side Chain
 β C
 α C
 6 — 2 — 3 — 1 — 5 — 4 — OH — OC_2H_5 ← Methoxyl Group
 ← Phenolic Hydroxyl

Notes

Phenylpropane Unit } Common Names
C9

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Lignin Structure Methoxyl Content

Lignin Source	Grass	Softwood	Hardwood
p-Coumaryl Alcohol (No Methoxyl)	10-25%	0.5-3.5%	Trace
Coniferyl Alcohol (1 methoxyl)	25-50%	90-95%	25-50%
Sinapyl Alcohol (2 Methoxyls)	25-50%	0-1%	50-75%

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Lignin Biosynthesis Nomenclature

R
 OH
 p-Hydroxyphenyl

R
 OH OCH_3
 Guaiacyl

R
 OH OCH_3 OCH_3
 Syringyl

- Once incorporated into lignin, the ring structures of the precursors are given these names.

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Lignin Biosynthesis
Enzymatic Formation of Phenoxy Radical

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- The initial step in the polymerization of lignin is an enzymatic directed one electron abstraction forming a phenoxy radical.

Enzyme

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Lignin Biosynthesis
Resonance Forms of Phenoxy Radical

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- The phenoxy radical is only one of several resonance structures.
- This figure shows a second resonance structure with the free radical on the 5 carbon of the ring.

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Lignin Biosynthesis
Resonance Forms of Phenoxy Radical

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Lignin Coupling
 β -O-4

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β -O-4 Linkage

Notes

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