Wood Chemistry

Wood Chemistry
PSE 406 / Chem E 470

Lecture 10
Lignin Biosynthesis II

Wood Chemistry

Class Agenda

- Dehydrogenation lignin (Test Tube)
- Possible linkages
- Free radical coupling example
- Isolation of lignin
- Linkages
  - ≈ β–O–4, 4–0–5, 5–5, β–β, β–5, β–1
- Appendix (coupling mechanisms)

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Summary of Last Lecture

- In the last lecture, we reviewed the results of a large amount of research into the formation of lignin precursors in the tree. We also discussed possible free radical reaction sites on these molecules. It is known that these precursors will couple forming linkages. This can be done in a test tube. The question is what happens in the tree?

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Test Tube Lignin

- Lignin precursors have been reacted with free radical initiators such as horseradish peroxidase in order to induce free radical coupling.
- Analysis of the resulting material (dehydrogenation lignin) has given information on the nature of the bonds formed.
- Two ways of adding precursors:
  - » Zulaufverfahren (one time addition of monomer)
  - » Zutropfverahren (slow addition of monomer)
  - » These 2 methods significantly change the linkages formed.

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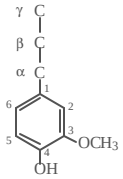
Possible Lignin Linkages

- If you look at this precursor, you can see (ignore the 3 position) that there are several possible linkage combinations. Not all of these occur.



Possible Combinations

β	1	4-O	5
β-1	1-0-4	4-O-5	5-5
β-O-4	1-5	4-O-O-4	
β-5	1-1		
β-β			

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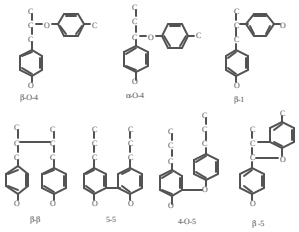
Common Lignin Linkages

- The linkages shown on the right are those formed in dehydrogenation polymers and also found in wood. All but the α-O-4 linkage are formed through free radical coupling.



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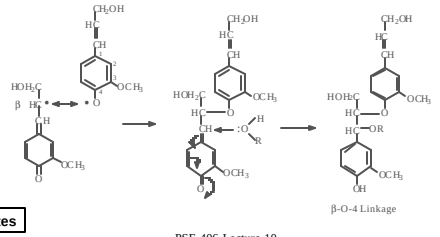
Lignin Coupling Example: β-O-4

- Here is an example of a coupling mechanism. Additional examples can be found in the appendix.



β-O-4 Linkage

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How Do We Know What Linkages are Found in Actual Lignin?

- In order to study lignin, we need to isolate it.
  - » Isolation procedures modify lignin structure.
  - » It is not possible to isolate all of the lignin.
  - » As a polymer, it is difficult to determine all of the structural elements
- Analysis of lignin after isolation:
  - » Use of polymer analytical techniques (H^1NMR, C^{13}NMR, IR, UV,etc.)
  - » Break the lignin into fragments, analyze the fragments, and put the puzzle back together.

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Lignin Isolation Procedures

- Insoluble Lignin Preparations: Klason, Cuoxam, Periodate, etc
  - » Destruction of carbohydrates with acids, enzymes, etc: Lignin structure highly altered.
- Soluble Lignin Preparations: Bjorkman (MWL), Brauns, etc
  - » Lignin is removed from wood (solublized) using different solvents and mechanical techniques. These materials are considered most representative of native lignin (MWL #1). Very low yields.
    - – Neutral Solvents (Example: MWL, ball milling → dioxane extraction
    - – Acidic Organic Solvents (Example: Alcohol lignin)
- Commercial Lignin Preparations
  - » Highly degraded materials including Kraft lignin, lignosulfonates, hydrolysis lignin, etc.

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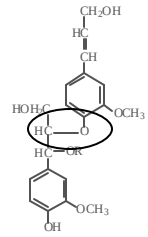
Lignin Linkages: β-O-4

- Easily the most prevalent linkage.
  - » Roughly 50% of softwood lignin linkages.
  - » As high as 60% in hardwood lignin.
- Dimer structure name:
  - » Aryl glycerol β-aryl ether
- Reactive linkage in alkaline pulping systems



β-O-4 Linkage

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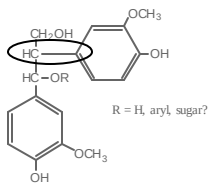
Lignin Linkages: β-1

- Minor linkage: estimates range between <2 to 7% in softwood lignin.
- Dimer structure name:
  - » 1,2-Diaryl propane
- Formation of this linkage requires a splitting off of one of the side chains (see next slide).



R = H, aryl, sugar?

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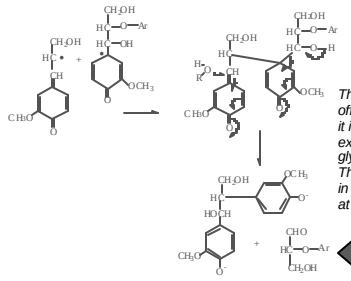
Displacement of Side Chain in β-1 Formation



The side chain which is split off in this coupling reaction if it is attached b-O-4 as in this example is known as: glyceraldehyde-b-aryl ether. The amount of this structure in softwood has been estimated at 2%.

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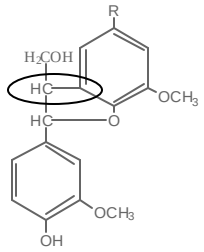
Lignin Linkages: β-5

- 7-12% of softwood linkages
- ~5% of hardwood linkages
- The cyclic type of β-5 linked structure shown on the right is known as:
  - » Phenylcoumaran
- The are a small amount of non-cyclic β-5 structures.
- Notice that this dimer also contains a α-O-4 linkage



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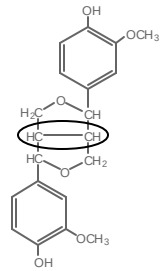
Lignin Linkages: β-β

- Very minor component in hardwoods and softwoods (2 - 3%)
- Dimer structure name:
  - » Pinoresinol
  - » The structure on the right is a wood extractive



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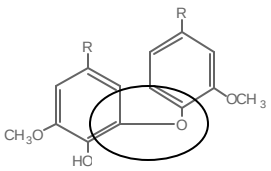
Lignin Linkages: 4–0–5

- Linkage makes up roughly 4% of softwood and 7% of hardwood linkages.
- Dimer structure name:
  - » Diaryl ether
- Even though this is an ether linkage, it is not cleaved under pulping conditions.



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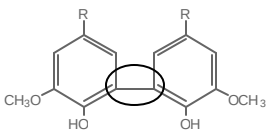
Lignin Linkages: 5–5

- The amount of 5-5 linkages in lignin is debated.
  - » ~ 10- 13 % in softwoods
  - » ~5% in hardwoods
- Dimer structure name:
  - » Biphenyl
- Even though this is an ether linkage, it is not cleaved under pulping conditions.



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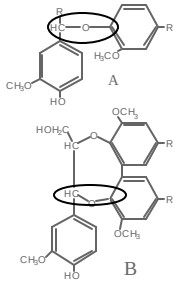
Lignin Linkages: α–O–4

- There are 3 possibilities for α-O-4 linkages
  - » Phenylcoumarin structures (β-5)
  - » Free α-O-4 (Structure A)
  - » Eight membered ring
    - – NMR work by Brunow indicates that there are essentially no free α-O-4. All of these linkages are linked to biphenyl structures (5-5). (Structure B)



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Summary of Lignin Linkage Frequencies

Linkage	Dimer Structure	Softwood %	Hardwood %
β-O-4	Arylglycerol-β-aryl ether	50	60
α-O-4	Noncyclic benzyl aryl ether	2-8	7
β-5	Phenylcoumaran	9-12	6
5-5	Biphenyl	10-11	5
4-0-5	Diaryl ether	4	7
β-1	1,2 Diaryl propane	7	7
β-β	Linked through side chains	2	3

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Lecture 10 Appendix

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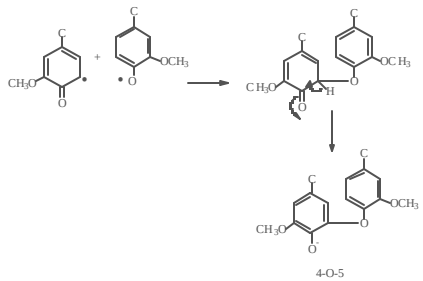
Lignin Coupling
4-O-5



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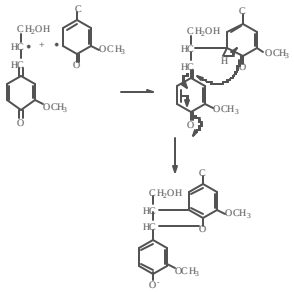
Lignin Coupling
β-5



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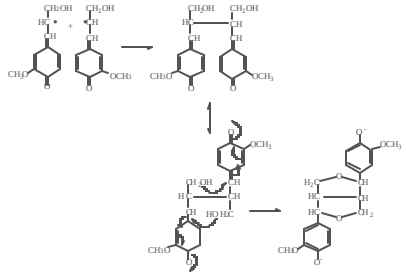
Lignin Coupling
β–β



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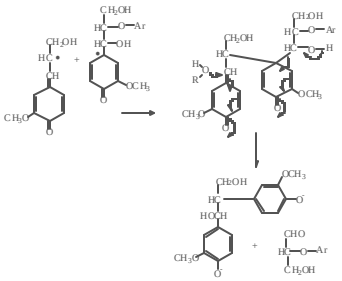
Lignin Coupling
β-1



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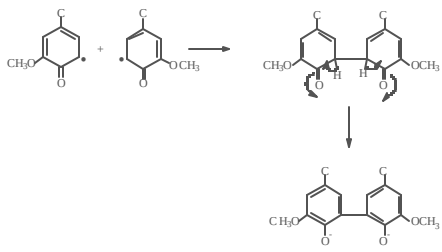
Lignin Coupling
5-5



5-5