Chemistry of biomass

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Outline

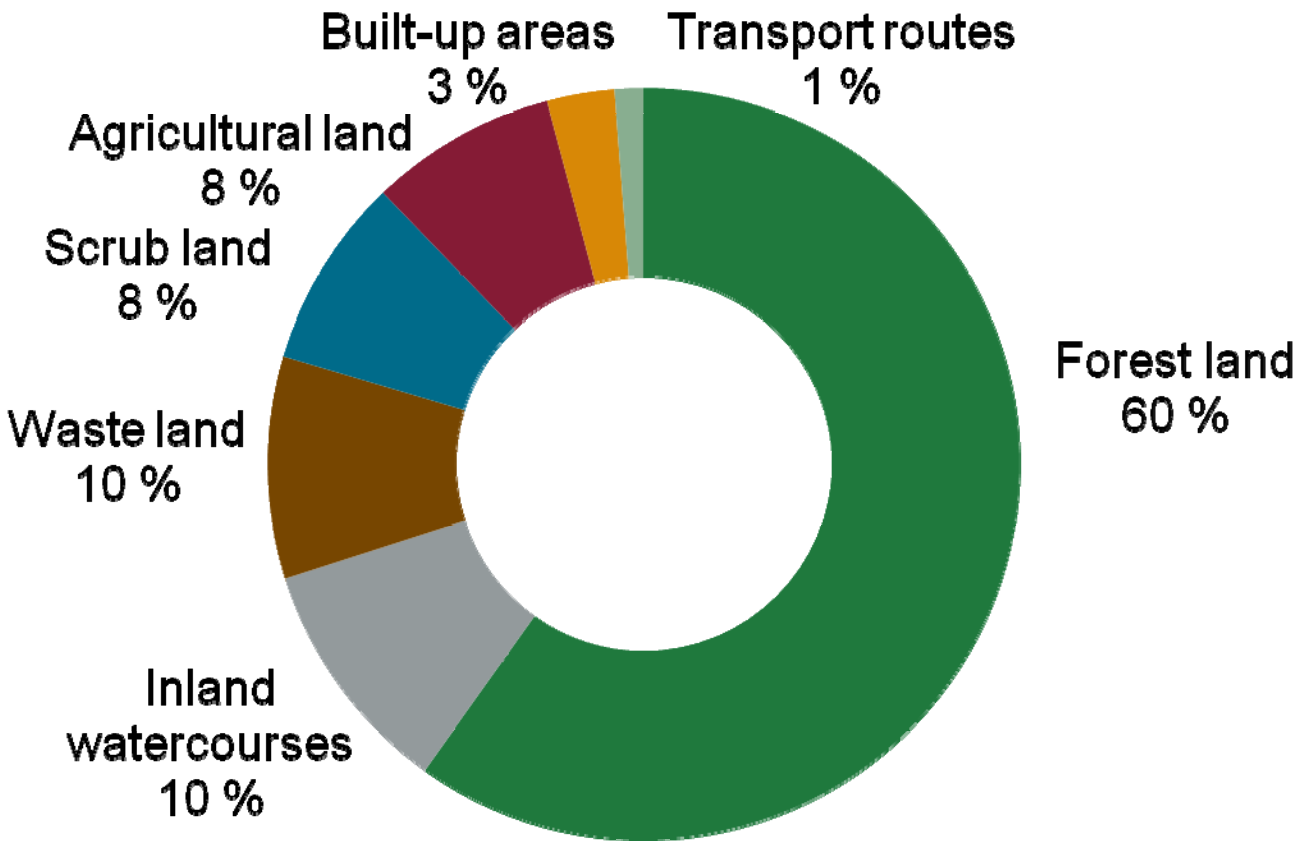
- Introduction
- Structure of
  - Cellulose
  - Hemicelluloses and pectins
  - Lignin
  - Extractives

Different types of biomass

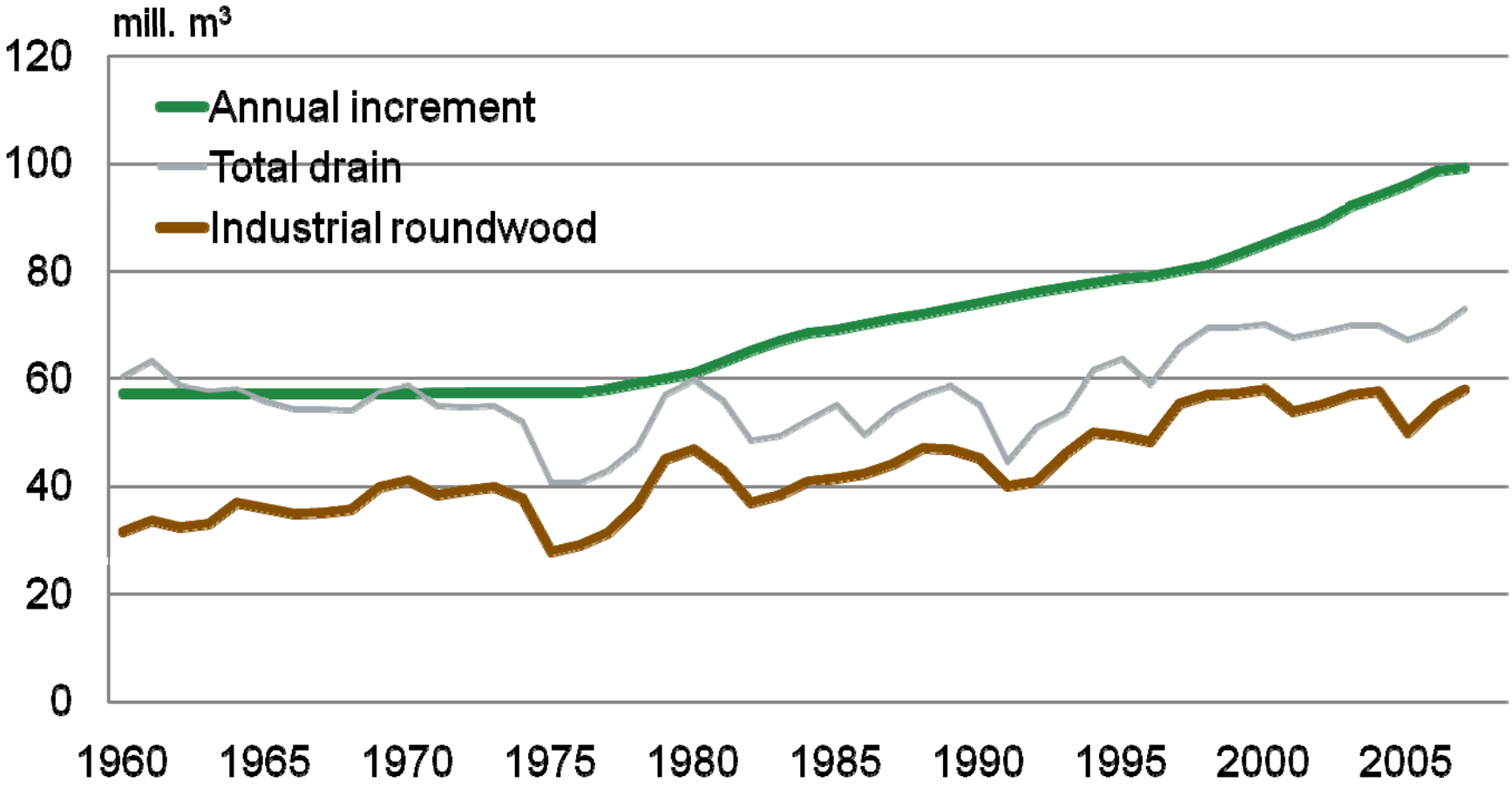
- Wood
- Bark, leafs, needles
- Plant material
- Agricultural waste
- Etc.

Forests cover 60% of the area in Finland

Total area in Finland 33.8 mill. ha



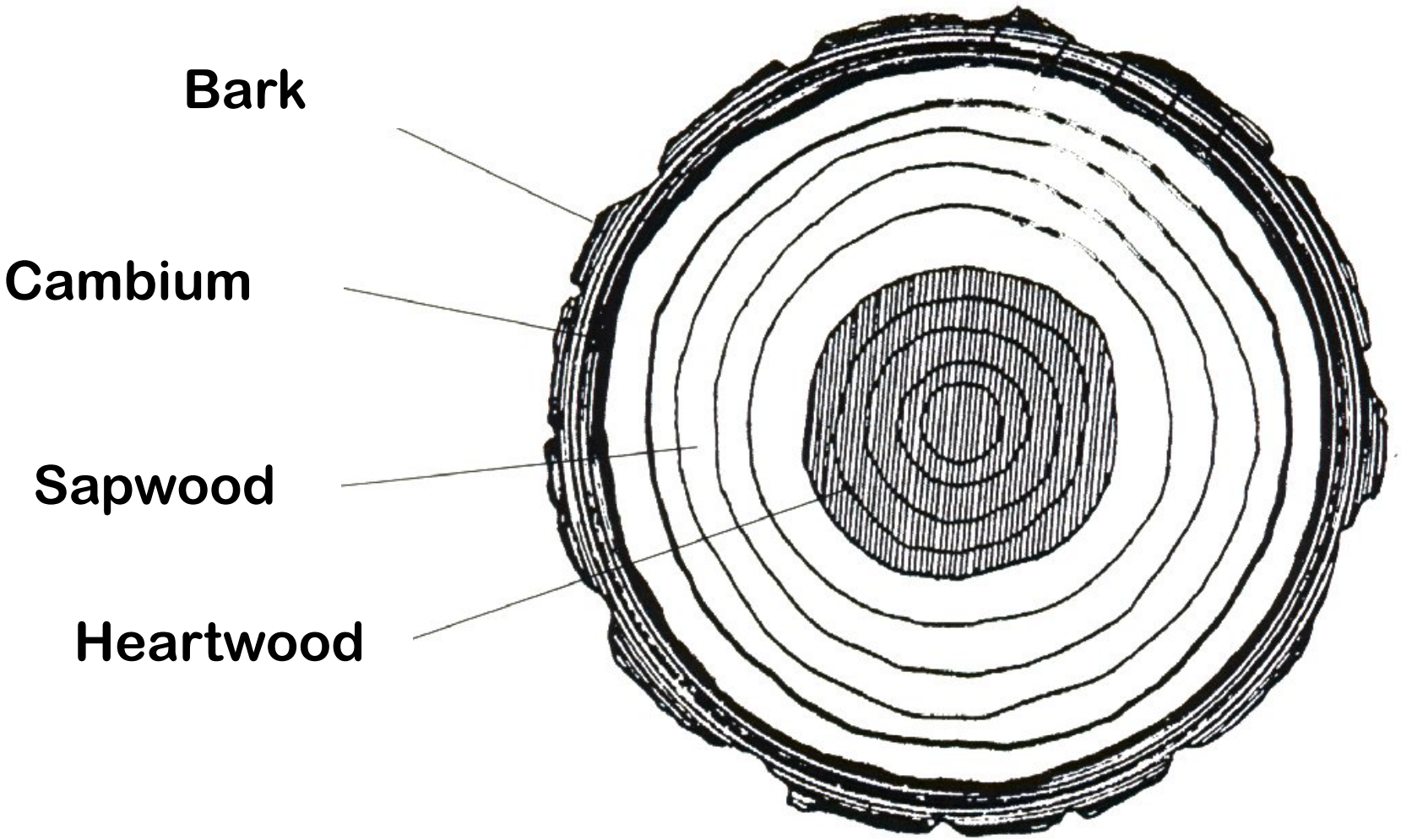
Forest balance in Finland 1960-2007



Forest reserves

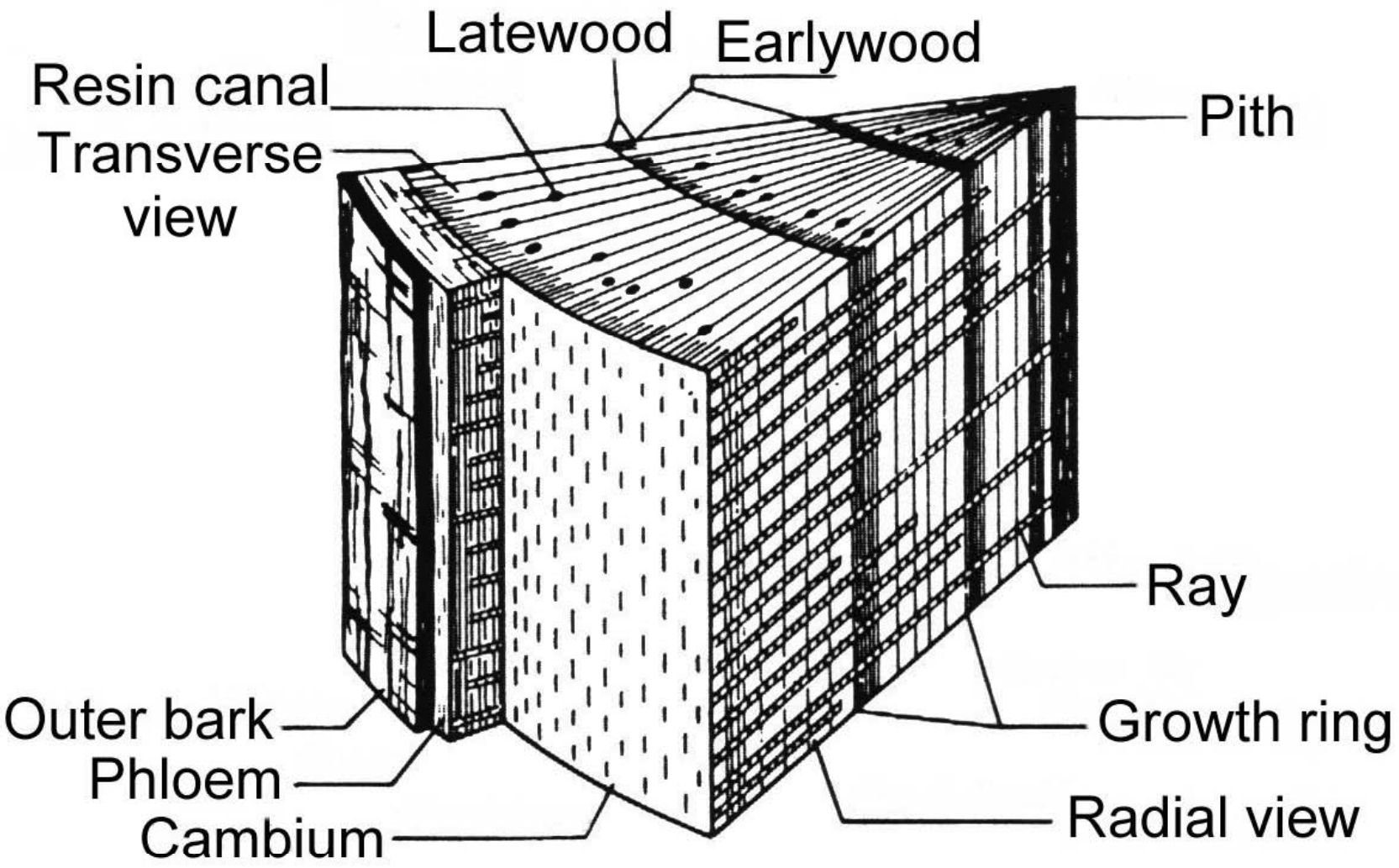
- Finland: Growth larger than harvesting
- Globally: Areas with a lack of fibres (south east Asia and western USA)
  - New fast growing species?
- Species
  - Globally: Softwood 1000, hardwood 30 000-35 000
  - Used commercially: USA 100, Europe 20
  - In Finland: 3 main species: spruce, pine and birch

Cross section of a tree

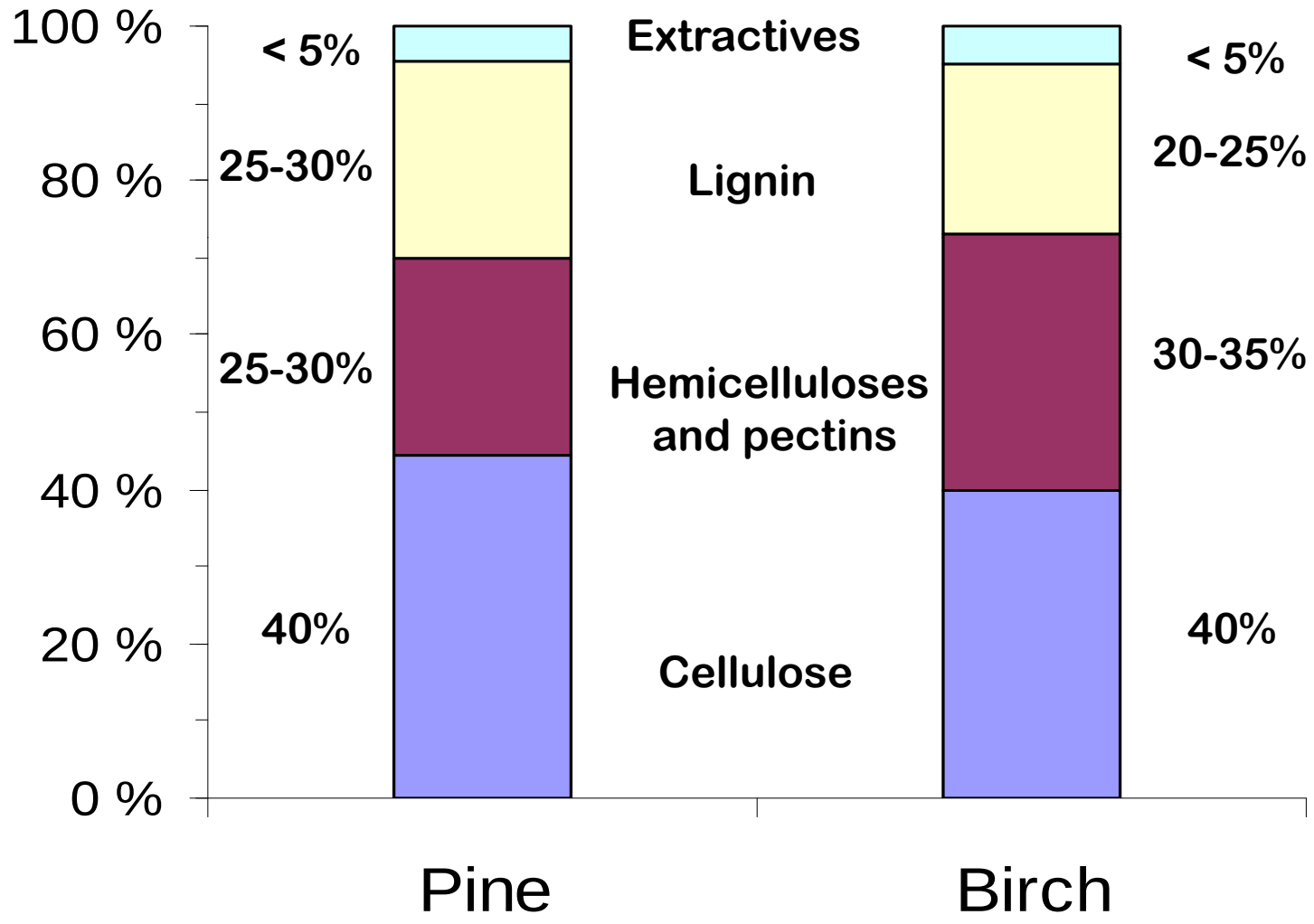


Macroscopical structure

- Bark (outer and inner)
  - Protection against mechanical injury and microbiological attacks
- Cambium
  - Thin layer of living cells
  - Cell division and radial growth
- Stemwood
  - Long cells, most of them vertically oriented
  - Support and storage of nutrients
- Pith
  - Soft tissue that are formed the first year


Latewood
Earlywood
Resin canal
Transverse view
Pith
Ray
Outer bark
Phloem
Cambium
Growth ring
Radial view

Chemical composition of pine (*Pinus sylvestris*) and birch (*Betula pendula*), % dry substance



Structure of cellulose

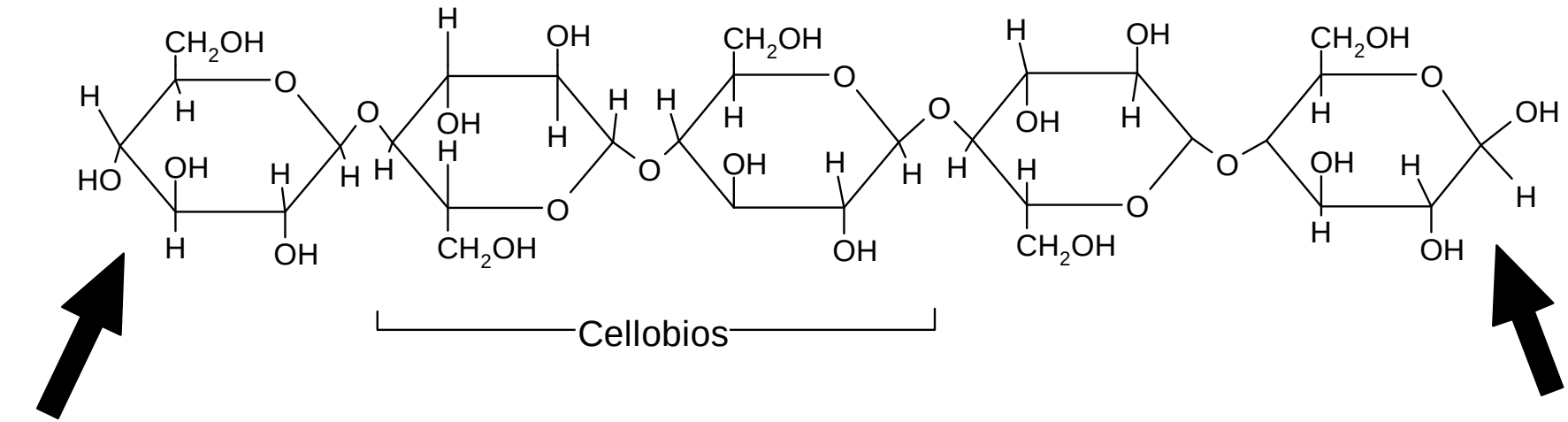
Cellulose, occurence

- “Backbone” in plants
- 95-99% in cotton, 20-30% in bacteria
- 40% of all plant-carbon is bound in cellulose
- Products: paper, film, additives, adhesives, textile fibres...

Molecular properties

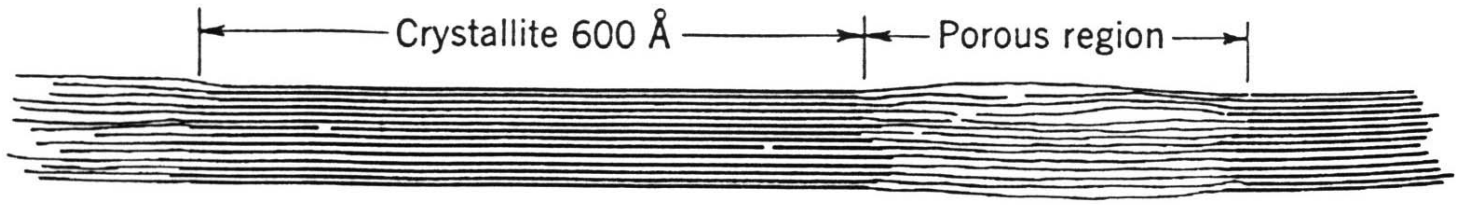
- Linear polymer - no branches!
- Homopolymer of β-D-glucopyranose units, linked by (1→4)-glucosidic linkages
- Every other glucose is up-side-down
- Repeating unit = cellobiose = 2 glucose units, length: 1.03 nm
- Insoluble in water

Cellulose chain



Hydrogen bonds

- Interactions between functional groups
  - In cellulose: OH and H
- Stabilising of molecule chains in ordered systems → supramolecular structure
- Enhances strength and changes the physical and chemical properties of the molecule
- Results in crystalline areas in cellulose



Structure of hemicelluloses and pectins

Hemicelluloses and pectins

- Heterogeneous group of heteropolysaccharides
- 20-30% of wood
- Support function
- Are easier to degrade by chemical treatments than cellulose
- Products: Emulsifiers, edible films, diatary fibres, pharmaceuticals, food additives, thickeners, gelling agents, adhesives, adsorbants, xylitol…

Building blocks

- Building blocks are different monosaccharides
  - pentoses (Xyl, Ara)
  - hexoses (Glc, Man, Gal)
  - hexuronic acids (GlcA, GalA, 4-O-meGlcA)
  - deoxyhexoses (Rha)
- Often branched
- Lower DP (100-300, cellulose about 10 000)
- Amorphous

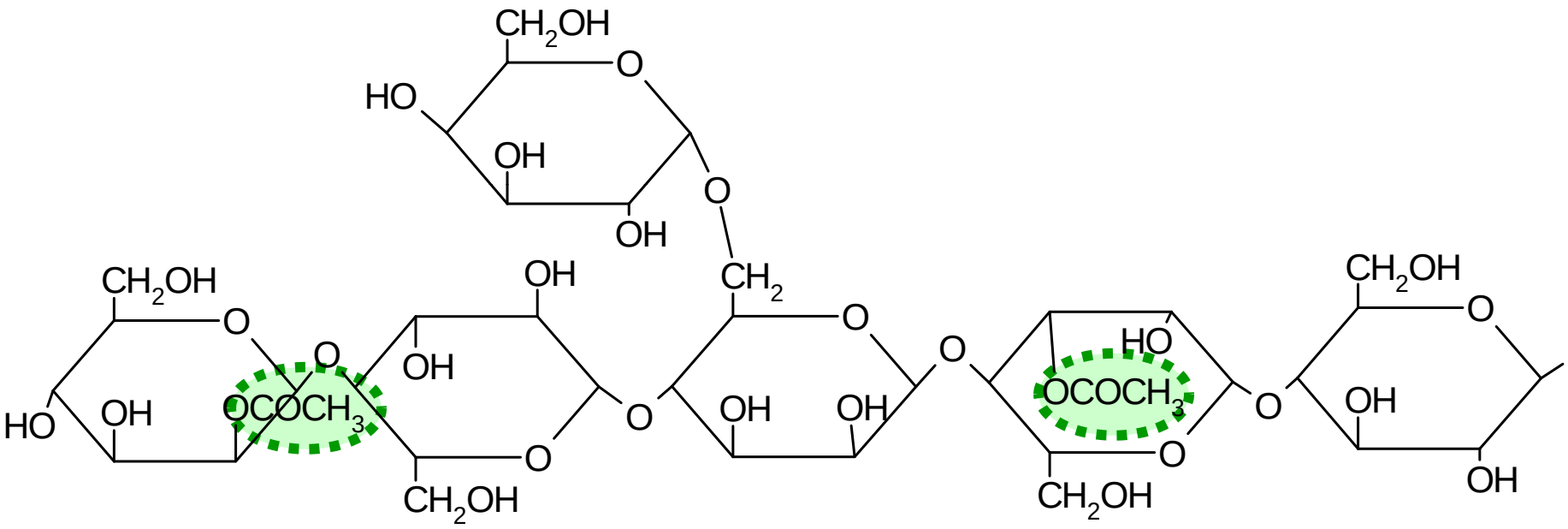
Common hemicelluloses:

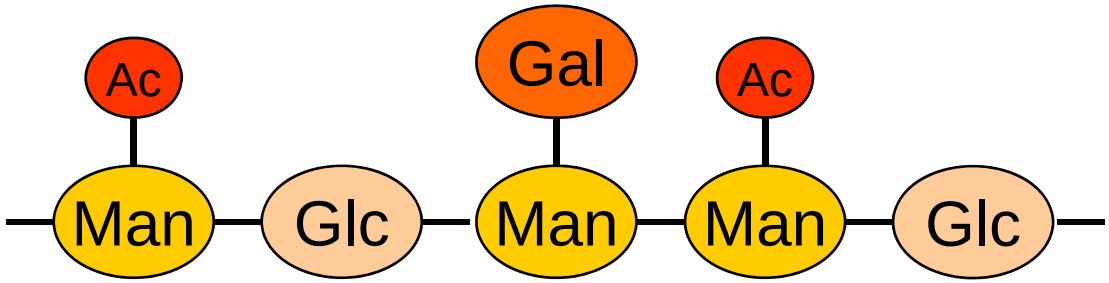
Name	Occur in	Yield %	Units	Molar ratio
Galactoglucomannan	Softwood	15-23	Man	4
			Glc	1
			Gal	0.5
			Acetyl	1
Arabinoglucuronoxylan	Softwood	5-10	Xyl	10
			4-O-MeGlcA	2
			Ara	1.3
Arabinogalactan	Larch	5-35	Gal	6
	Reaction		Ara	3
	wood		Glc	small
Glucuronoxylan	Hardwood	15-30	Xyl	10
			4-O-MeGlcA	1
			Acetyl	7
Glucomannan	Hardwood	2-5	Man	1-2
			Glc	1

Mannans

- Softwoods: O-acetyl-galactoglucomannans
  - 20-25%
  - Main chain: mannose and glucose
  - Side groups: galactose and acetyl groups
- Hardwoods: Glucomannans
  - Only 2-5%
  - Main chain: mannose and glucose
  - No side groups

O-acetyl-galactoglucomannans (GGM)

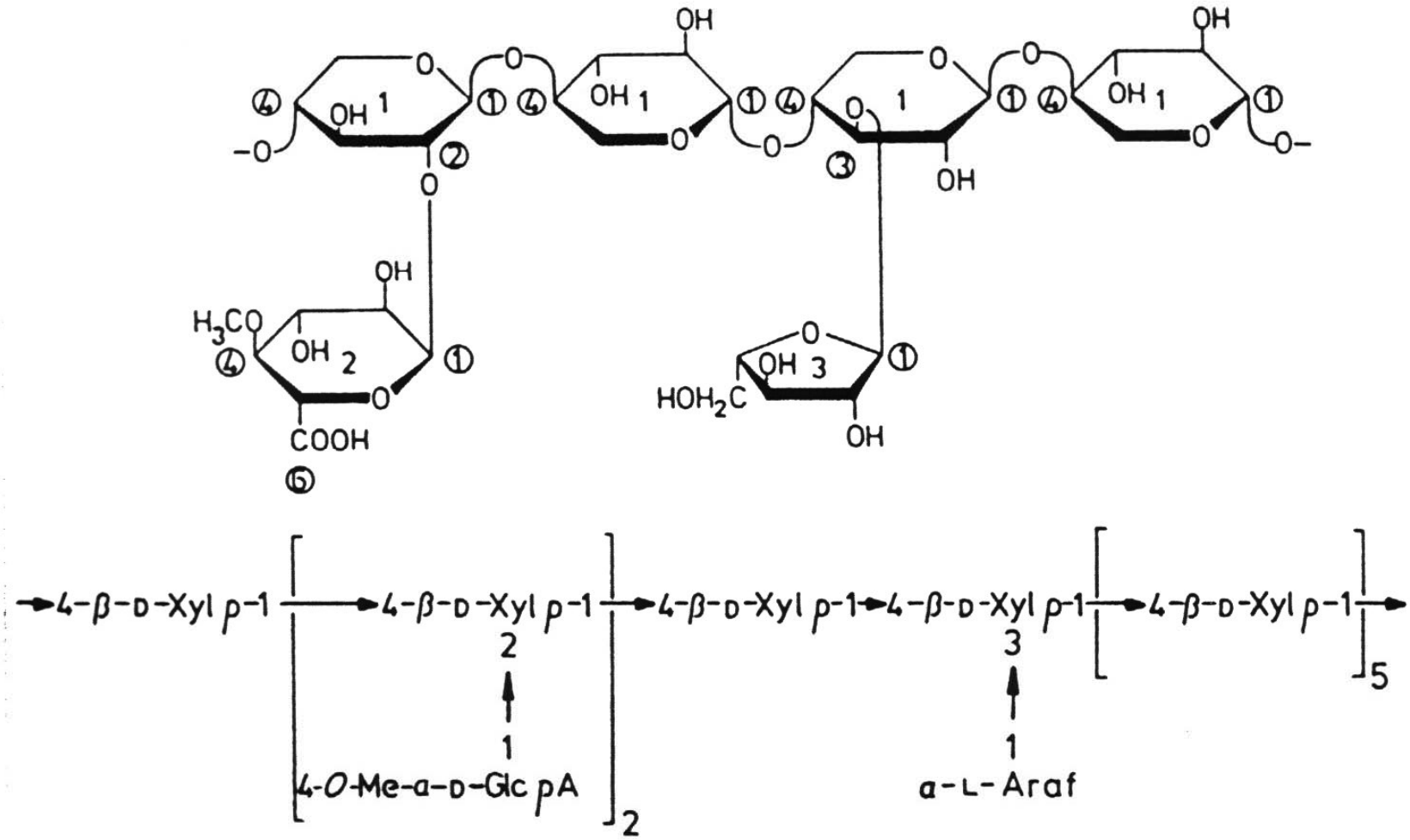




Xylans

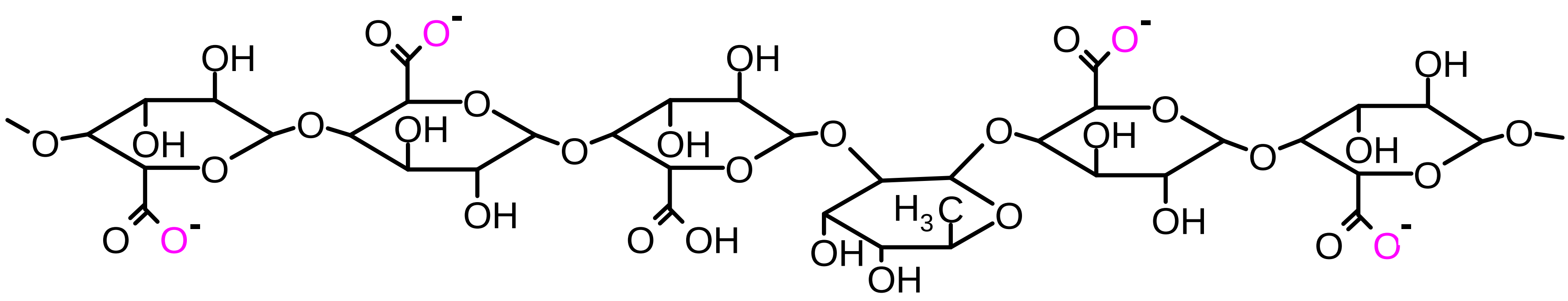
- Softwoods: arabino-4-O-methylglucuronoxylan
  - 5-10%
  - Main chain: xylose
  - Side groups: 4-O-methylglucuronic acid and arabinose
- Hardwoods: O-acetyl-4-O-methylglucuronoxylan
  - Dominating hemicellose, content 15-30%
  - Main chain: xylose
  - Side groups: 4-O-methylglucuronic acid and acetyl groups

Arabino-4-O-methylglukuronoxylan



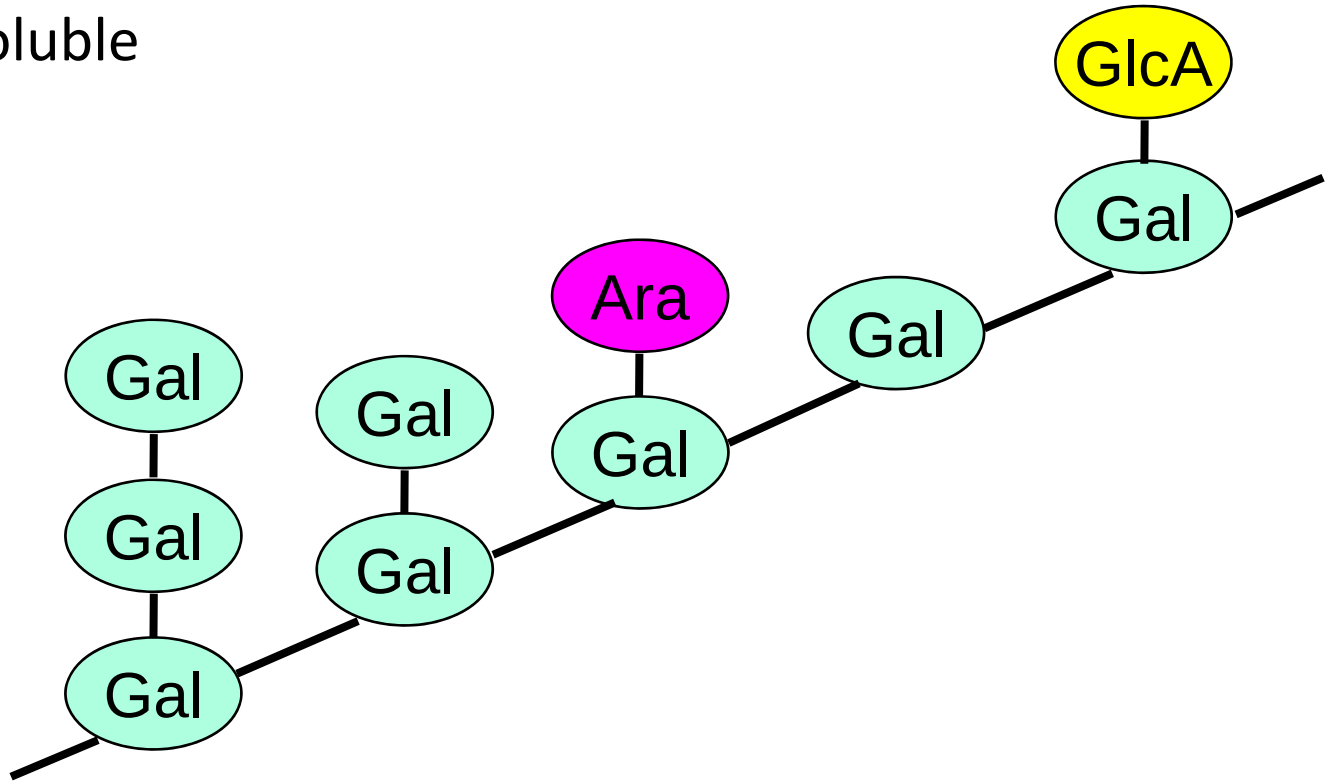
Pectins

- Located mainly in ML and P
- Main chain: galacturonic acid and rhamnose
- Methylesterified to high degree (spruce)
- Alkaline treatment → anionic pectic acids
  - Used as thickeners

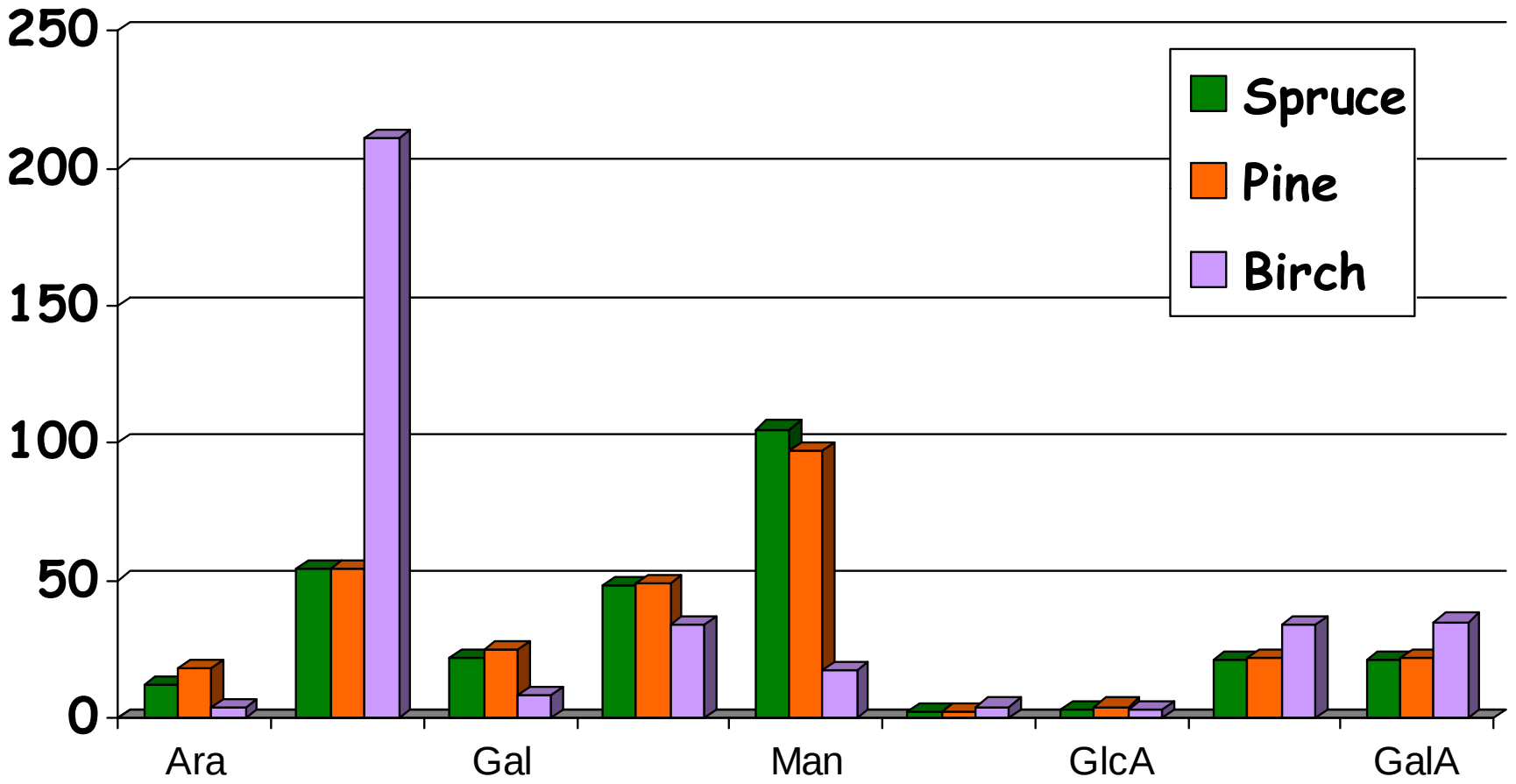


Arabinogalactans

- Found in heartwood of larch and in compression wood
- Branched
- Water soluble



Sugar units in different species



Starch

- Especially in plant material
- Consists of glucose units
- Two types of polymers
  - Amylose: α-linkages → helical chains
  - Amylopectin: α-linkages + braches

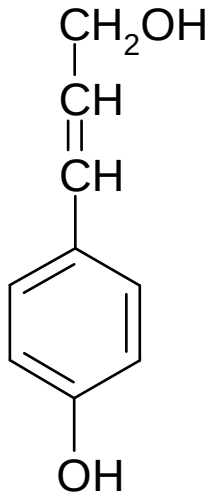
Structure of lignin

Occurrence

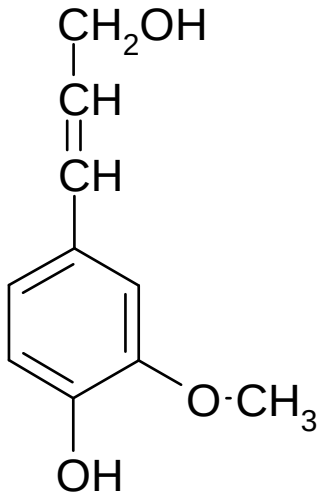
- Three dimensional, amorphous polymer
- Formed after synthesis of polysaccharides → strong fibres
- Occur only in higher plants
  - No lignin in primitive plants (algae, fungi and lichens)
- Lignin content 20-40%
- Molar mass not known
- Bonds also between lignin and polysaccharides
- Products: adhesives, films with specific barrier properties, replace phenol formaldehyde resins in composites, road & soil dust control, etc.

Monomeric lignin structures

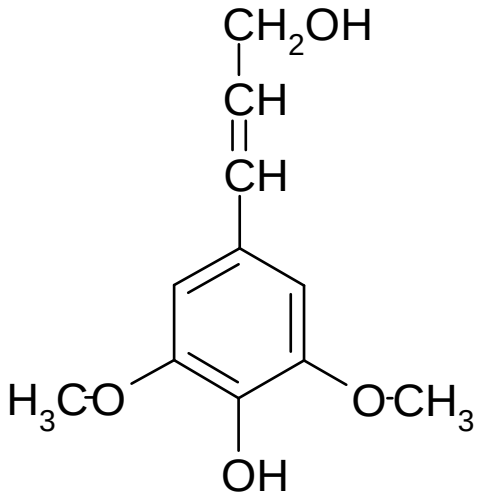
- Phenol + propane chain (3 carbons) = phenylpropane units
- Three different types occur:



p-coumaryl alcohol
(p-hydroxifenyl-)
Grasses



coniferyl alcohol
(guajacyl-)
Softwoods

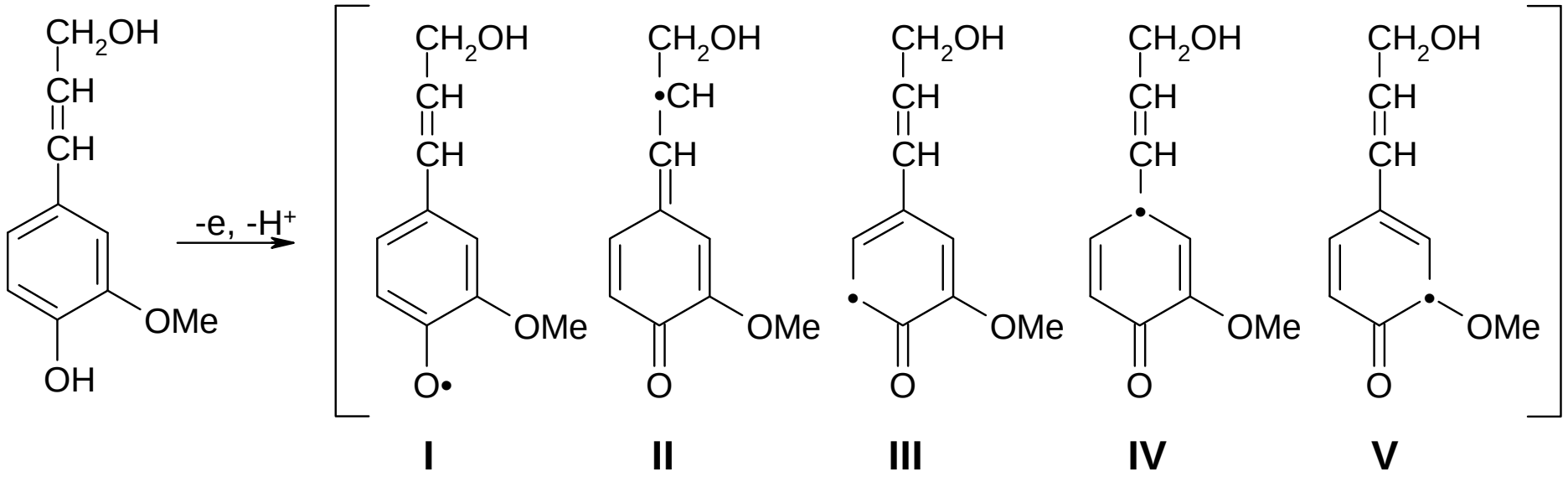


sinapyl alcohol
(syringyl-)
Hardwoods

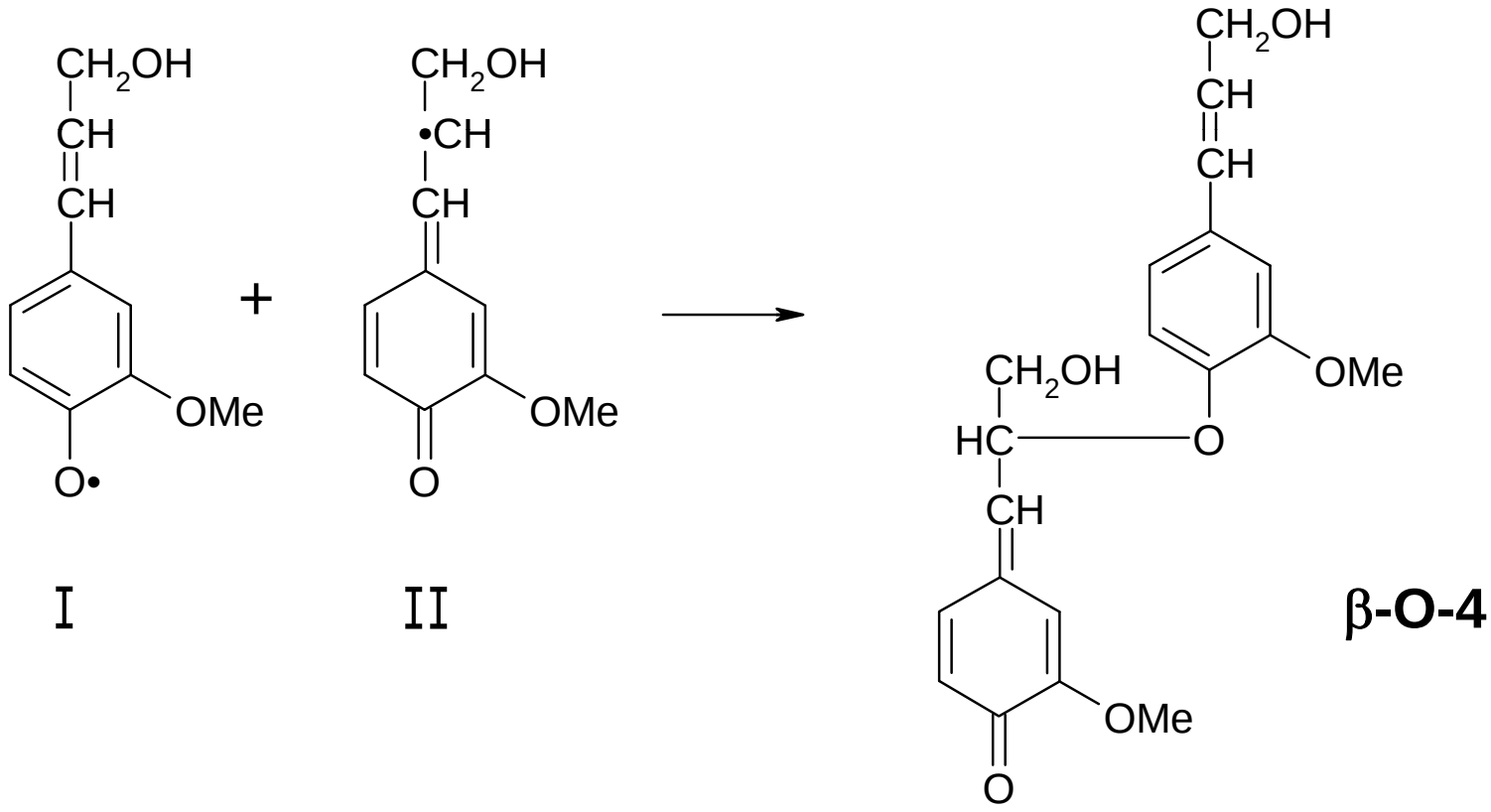
Polymerisation of lignin

- One-electron transfer by enzymatic dehydrogenation => 5 resonance-stabilized phenoxy radicals
- Polymerisation (no enzymatic control!!) via
  - Radical-radical coupling
  - Reaction between qinonmetide structures and free phenols or water

Phenoxi radicals



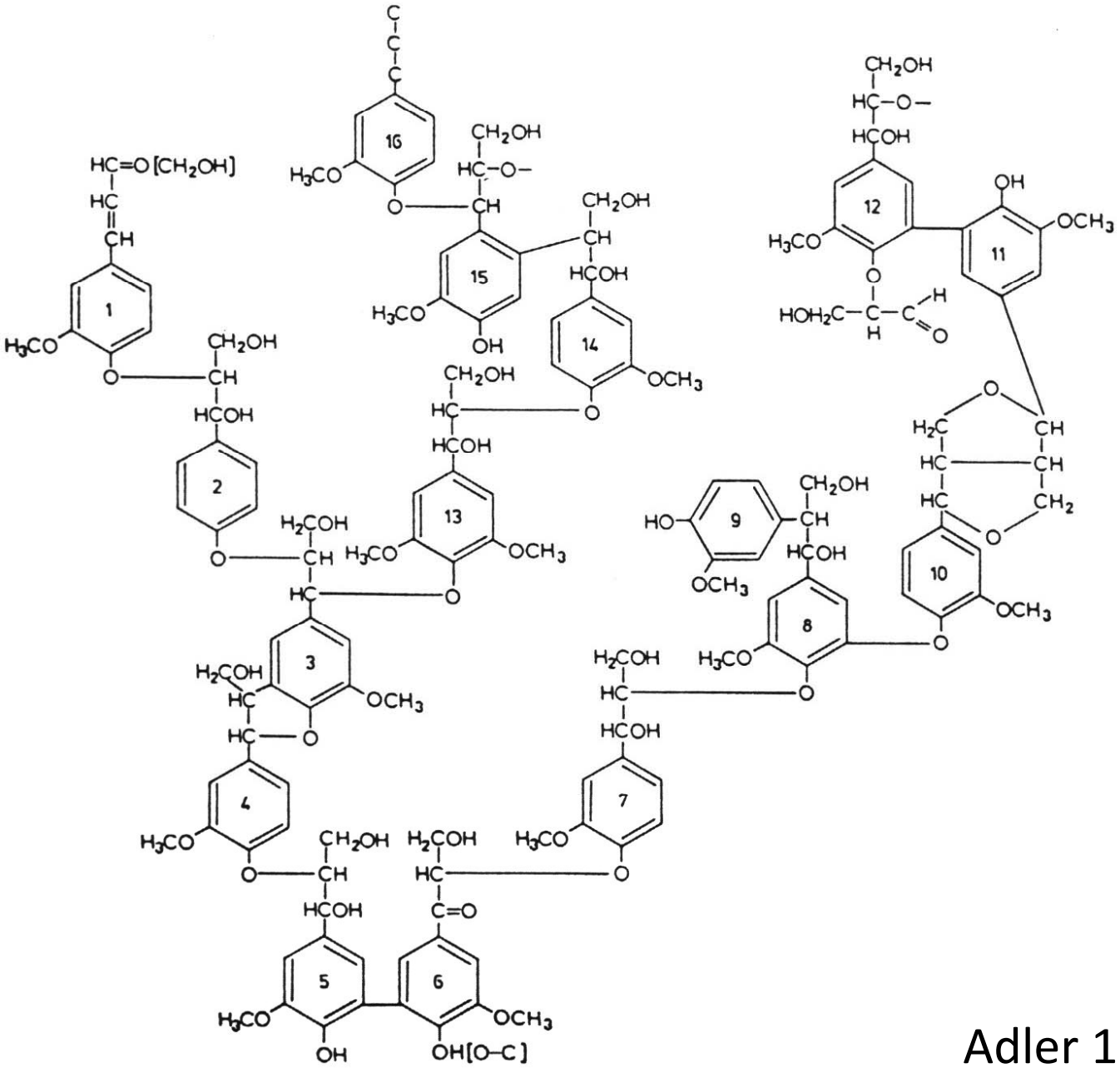
Radical-radical coupling



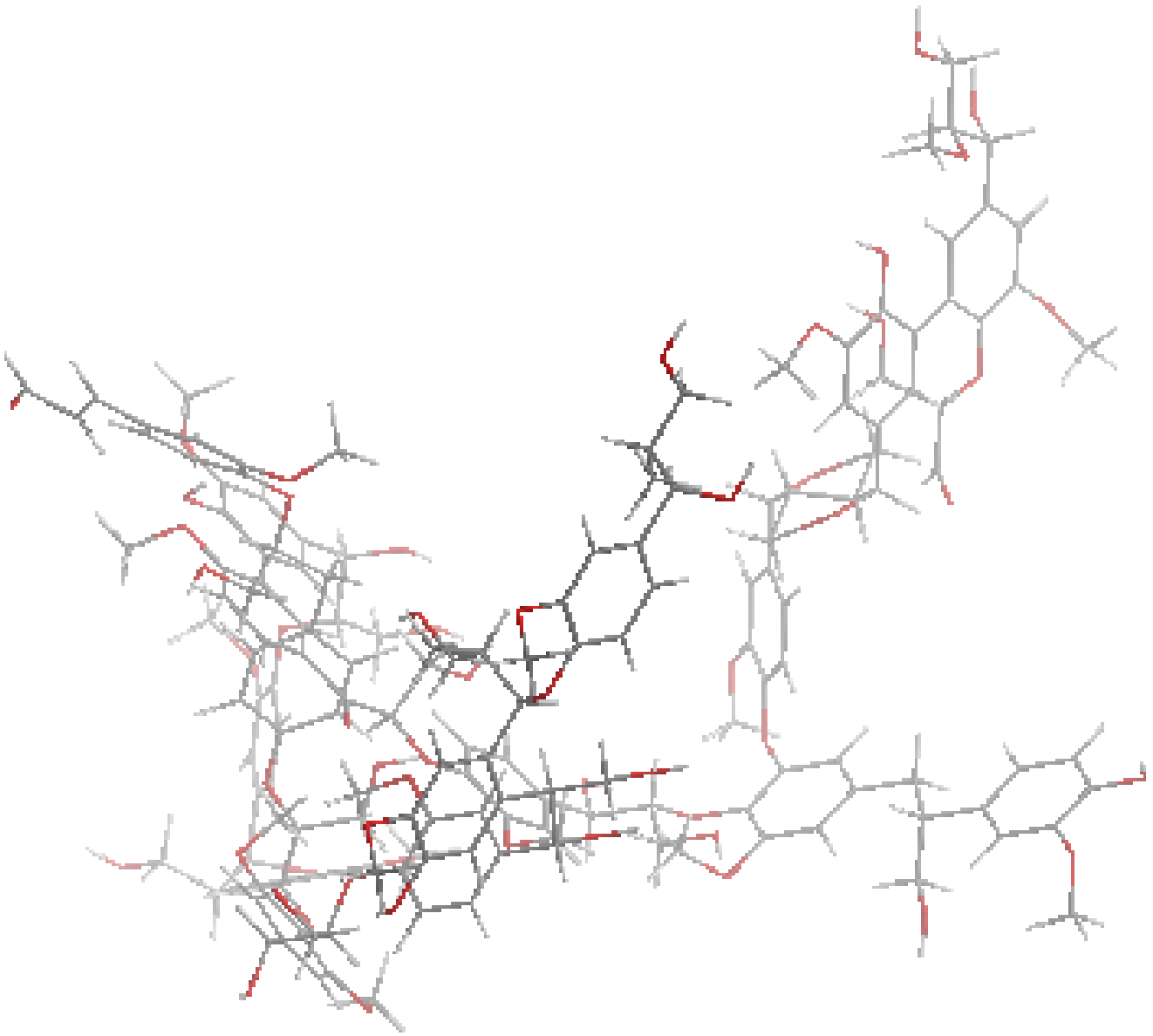
Continued polymerisation

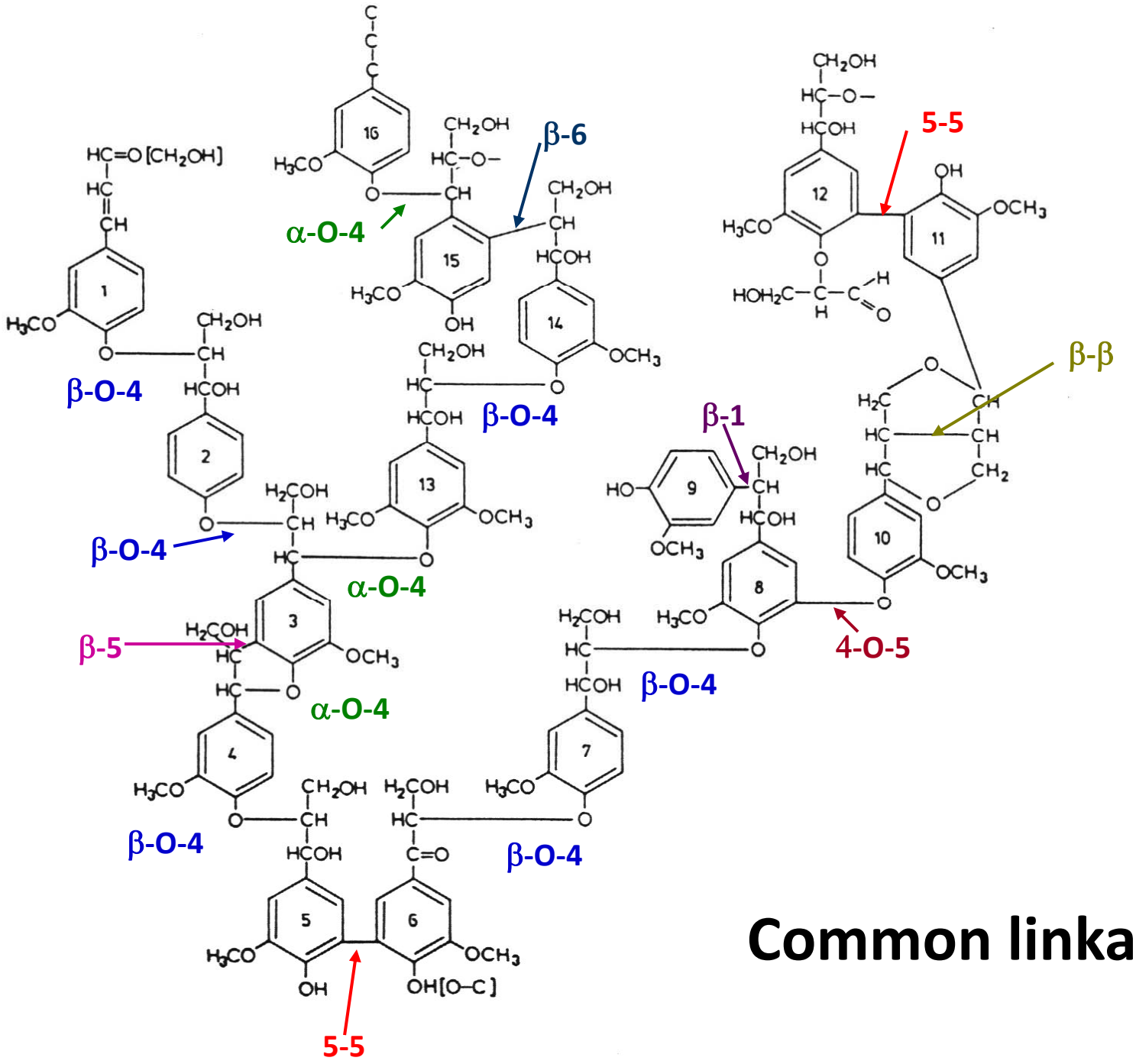
- Endwise polymerisation:
  - Coupling of monophenol to phenolic end group of di- or oligolignols
  - Coupling of two radicals of mono- and/or oligolignols

➔ Branched polymer

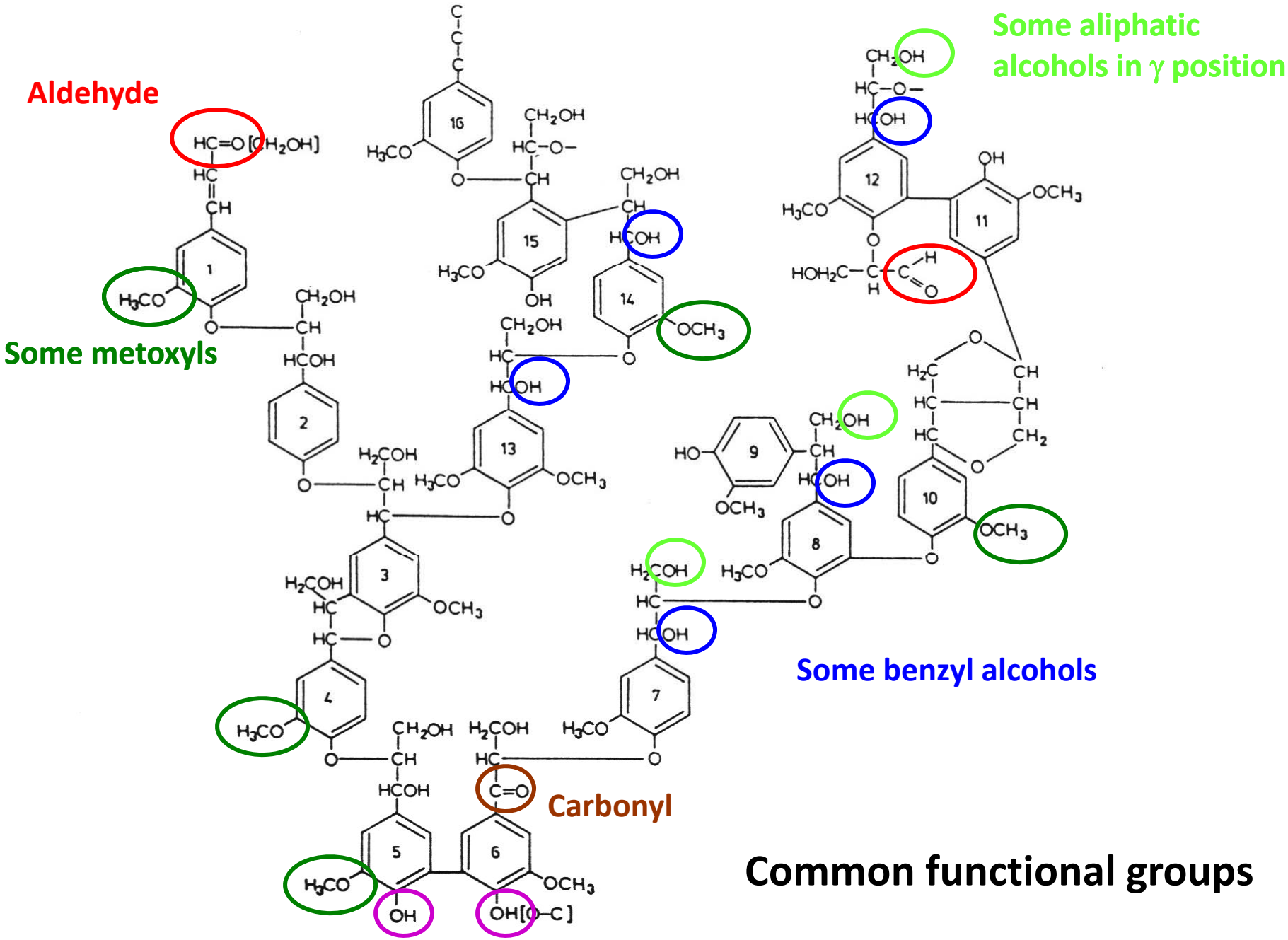


Adler 1977





Common linkages



Common functional groups

Structure of extractives

Classification

- Heterogeneous group of many compounds
- About 3-5% of the wood, lipophilic extractives about 1-2.5%
- Can be extracted from wood with solvents
  - Non-polar solvents ➔ lipophilic extractives
  - Polar solvents ➔ hydrophilic extractives
- Concentrated in resin canals (resin acids), parenchyma cells (fats) and heartwood (phenols)
- Raw material for chemicals as turpentine, tall oil and rosin, used as solvent, detergents, hydrophobation agents

Type	Occurrence	Example	Function	Polarity
Resin (oleoresin)	Resin canal	Monoterpenes Resin acids	Protection	Non-polar
Fats and waxes	Parenchyma cells	Triglycerides Sterylesters	Energy source Cell membrane	Non-polar
Phenols	Heartwood Knots	Lignans Stilbenes	Protection	Polar
	Bark	Flavonoids Tannins		
Sugars	Inner bark Cambium Ray cells	Mono- and di-saccharides Starch	Energy source	Polar
Salts	Water ducts	Ca^{2+}, K^{+}, Mg^{2+}, CO_3^{2-}, PO_4^{3-}	Biocatalysts	Polar

Lipophilic extractives

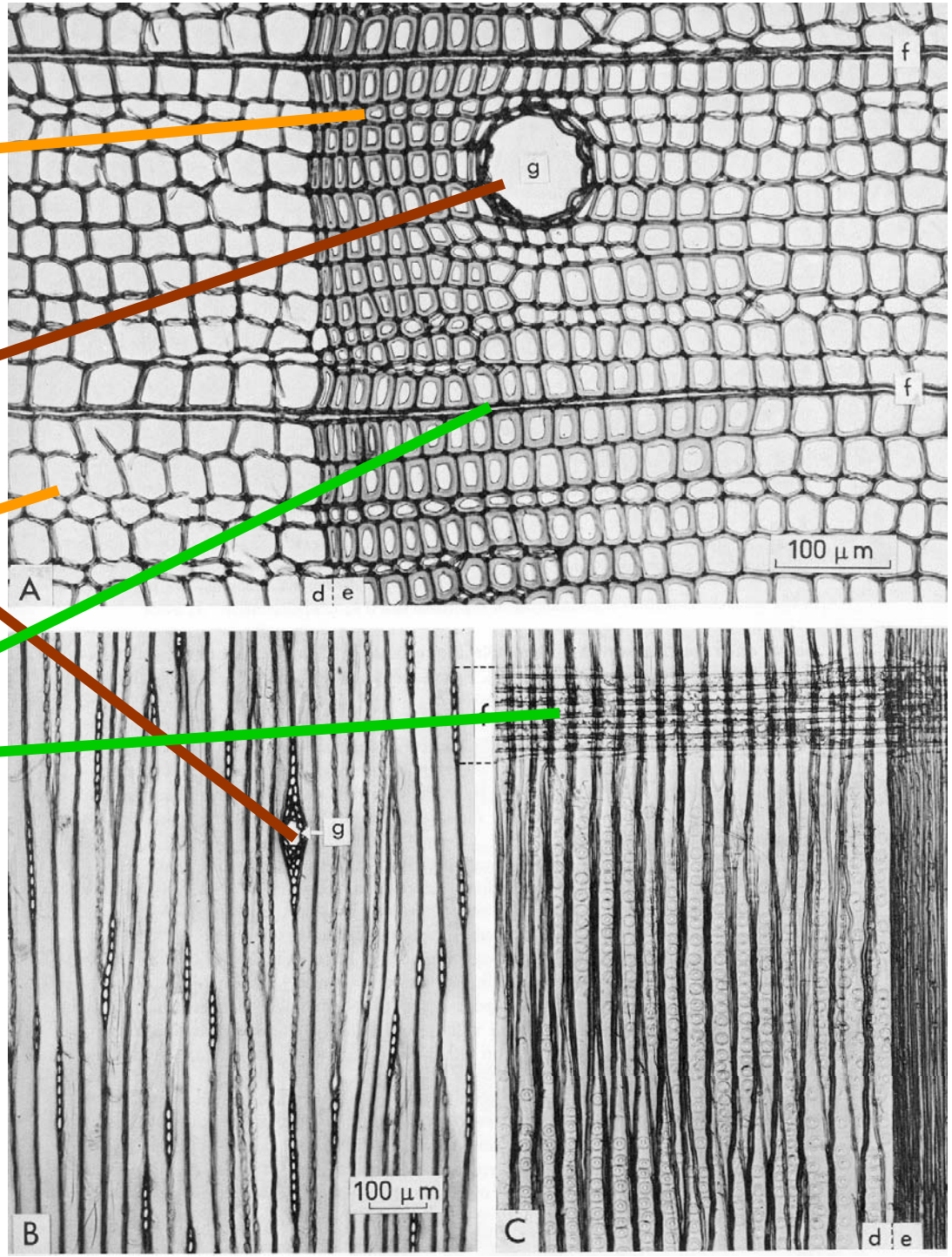
- Resin (Oleoresin)
  - Mainly of monoterpenes and resin acids
  - Found in resin canals
- Parenchyma resin
  - Fatty acids, triglycerides, sterols, alcohols, sterylesters…
  - Found in parenchyma cells

Latewood

Resin canal

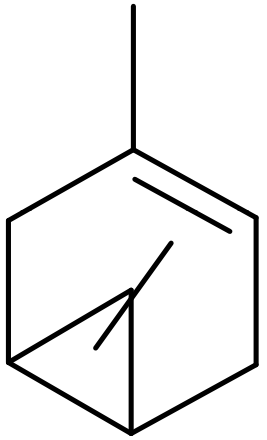
Earlywood

Ray cells



Monoterpenes

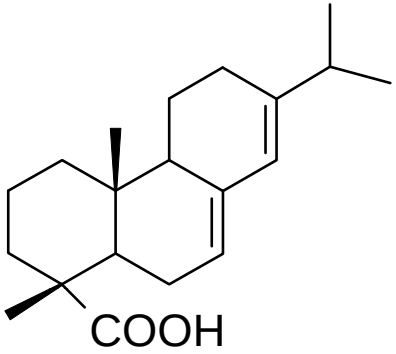
- Structure $C_{10}H_{16}$ (2 x C_5H_8)
- Volatile and contributes to the trees fragrance
- Occurs primarily in softwood resin
- Can be recovered as turpentine by steam distillation or from kraft pulp digester relief



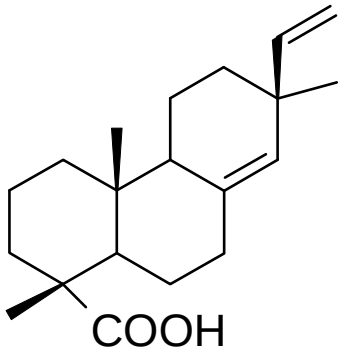
α-Pinene

Diterpenoids (e.g., resin acids)

- Only occur in softwoods
- 60-80% of the resin; 0.2-0.8% of the wood
- Abietane type: isopropyl or isopropenyl group at C-13
- Pimarane type: vinyl and methyl groups at C-13
- Surface active in soap form, can form micelles together with fatty acids
- Toxic to fish



Abietic acid



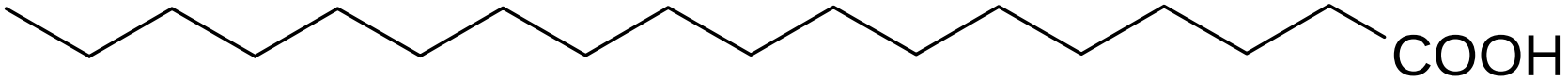
Pimaric acid

Parenchyma resin

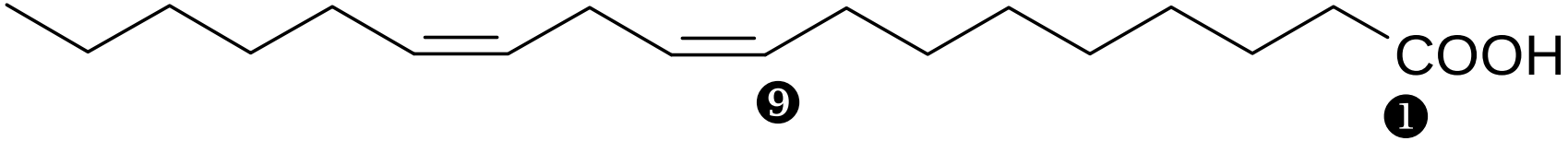
- Fats: esters of fatty acids with glycerol, primarily triglycerides
- Waxes: esters of fatty acids with alcohols, sterols and terpenalcohols
- Free fatty acids released from fats and waxes due to enzymatic hydrolysis after harvesting/heartwood formation

Fatty acids

- More than 30 have been identified in pine, spruce and birch
- Number of carbons: 16-22
- Saturated and unsaturated (in cis-form)
- Surface active and can be added to enhance washing of pulp (to remove neutral components)



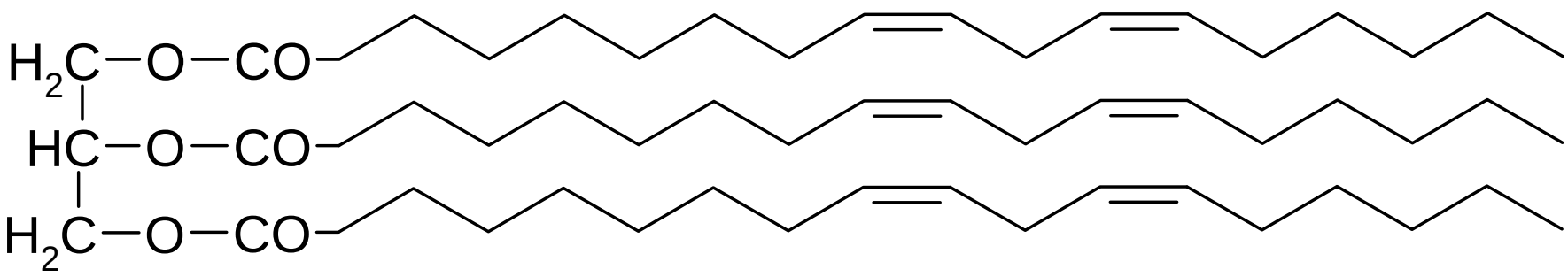
Stearic acid 18:0



Linoleic acid (9,12-18:2)

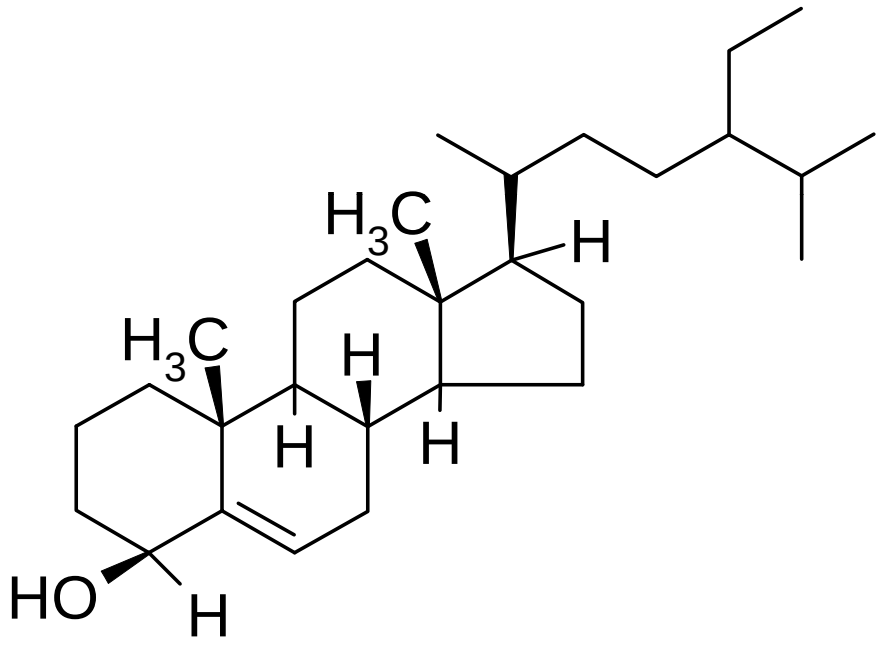
Triglycerides

- Glycerol + 1, 2 or 3 fatty acids
- Are found especially in parenchyma cells in fresh sapwood
- Hydrolysed in kraft pulping → release of free fatty acids



Alcohols/sterols

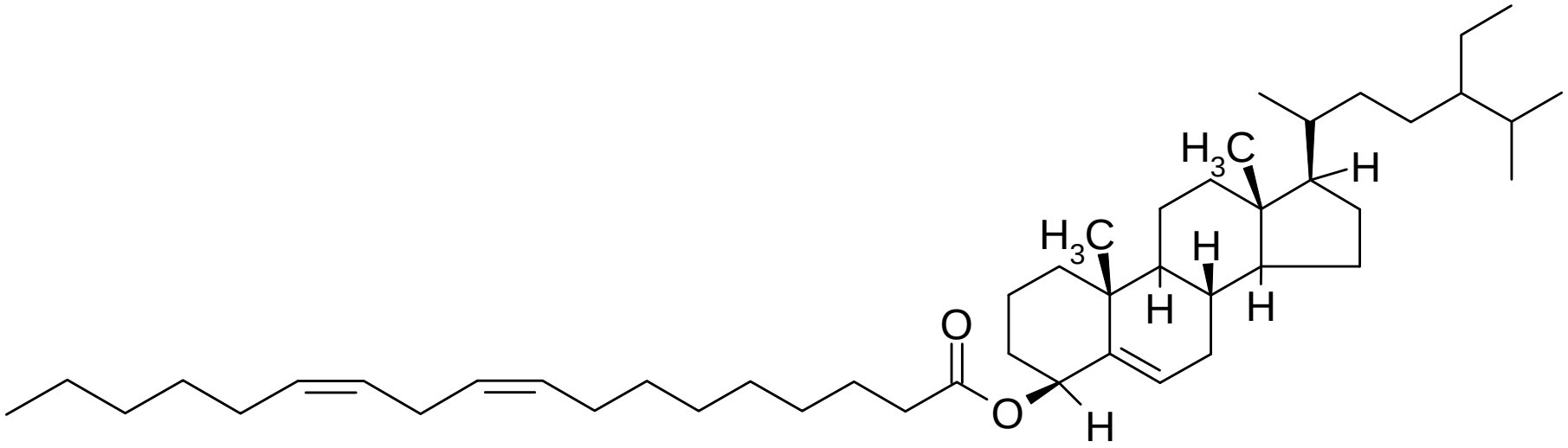
- Very hydrophobic due to their hydrocarbon structure
- Betulinol in birch bark (30%), protection function
  - Often remains in birch kraft pulp



β-sitosterol

Sterylesters (waxes)

- Sterol + fatty acids
- Hydrolysed in kraft pulping → release of free fatty acids



β-sitosterol + linoleic acid

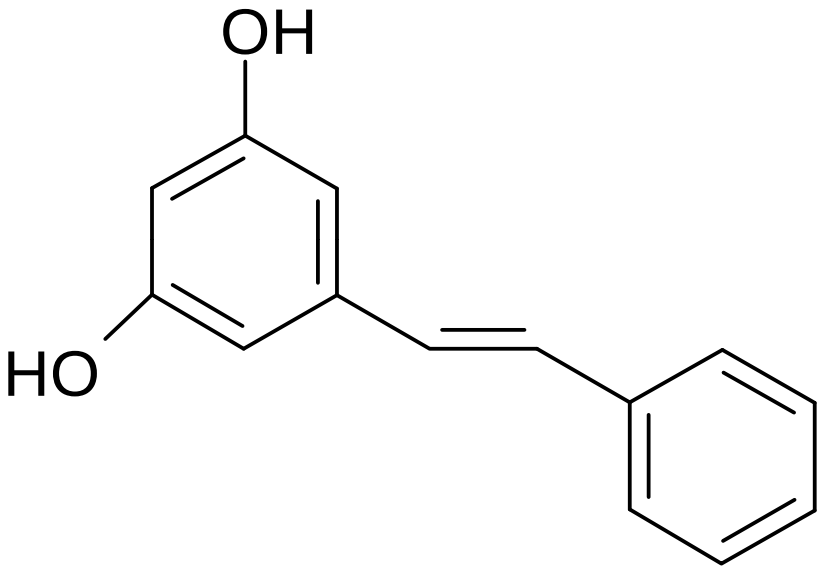
Phenolic substances

- Hydrophilic
- Found in bark and heartwood, only low contents in sapwood
- High contents in knots!
- Many substances; more than 1000 identified
- Function: protection against microbes
- Often coloured
- Products: antioxidants, food additives, dyes

Examples of phenolic substances

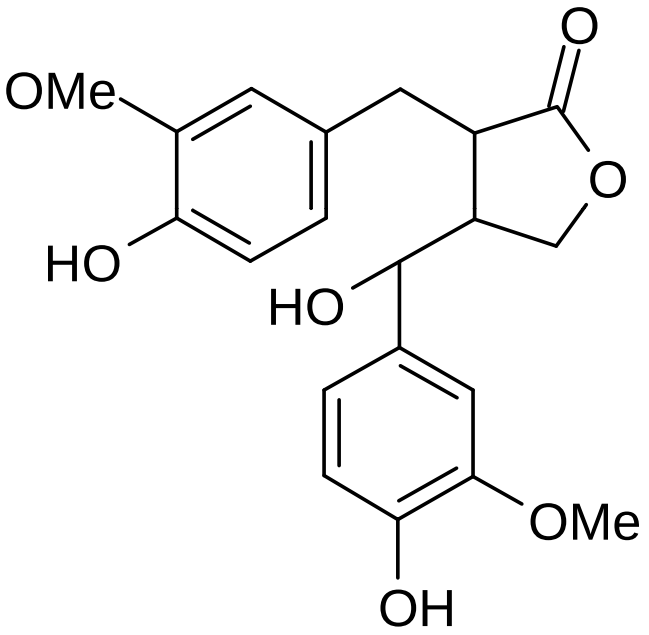
- Stilbenes: e.g. pinosylvin in pine
  - Antioxidant
- Lignans:
  - Formed by oxidative coupling of two phenylpropane units
  - Always contain a β–β bond
  - Knots can contain more than 10% HMR
  - Strong antioxidant
  - Anticarcinogenic
- Hydolyzable tannins (not common)
- Flavonoids, as chrysin (pine) and catechin
- Condensed tannins (polymers of flavonoids)

Stilbenes



Pinosylvin

Lignans

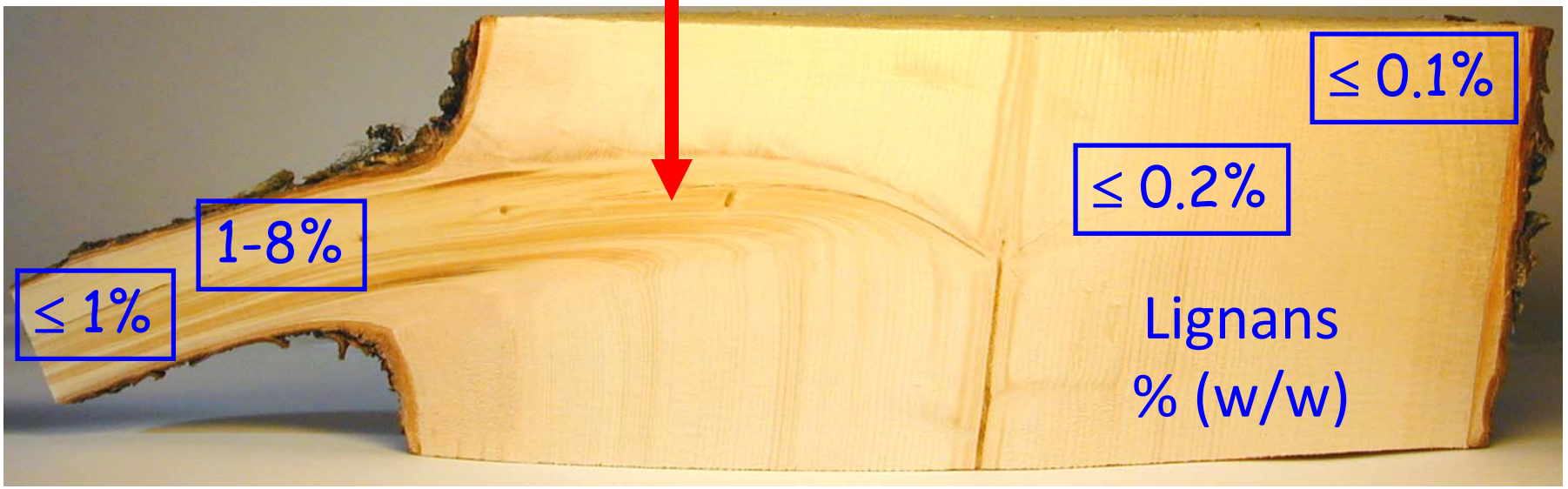


Hydroxymatairesinol

65-80% HMR

6-24%

30-500 times more lignans than in the stemwood!!!



Spruce knots are an exceptionally rich source of bioactive HMR

Willför 2002

Other phenolic substances

- Monomeric phenols
    - E.g. vanillin and coniferyl alcohol in spruce
- Polymeric phenolic substances
    - Occur in bark + in some hardwoods
    - Not lignin
    - E.g. esters with gallic acid
- Stilbenes in spruce bark
    - Can diffuse into the wood during storage and lower brightness of pulp

Mono- and disaccharides

- Found in the sap
- Glucose, fructose and sucrose (Glc + Fru)
- Glucosides, e.g., coniferin
- The content varies during the year (season variations)

Inorganic salts

- Higher contents in the leaves, needles and bark
- Important substances for the growing processes
- The content also depends on place of growth and climate
- Originates from salt that is deposited in the cells and sand (Si) that contaminates process
- Metal salts, carbonates, silicates, oxalates and phosphates
- Partly bound to carboxyl groups in xylans and pectins
- Deposits in recovery/burning (silicates), formation of ash when biofuels are used

Concentration of inorganic components in wood

Content, ppm	**Elements**									
400-1000	K	Ca								
100-400	Mg	P								
10-100	F	Na	Si	S	Mn	Fe	Zn	Ba		
1-10	B	Al	Ti	Cu	Ge	Se	Rb	Sr	Y	Nb
	Ru	Pd	Cd	Te	Pt					
0,1-1	Cr	Ni	Br	Rh	Ag	Sn	Cs	Ta	Os	
< 0,1	Li	Sc	V	Co	Ga	As	Zr	Mo	In	Sb
	I	Hf	W	Re	Ir	Au	Hg	Pb	Bi	

Repetition

- Cellulose
- Hemicelluloses and pectins
  - Mannans
  - Xylans
  - Pectins
  - Starch
- Lignin
- Extractives
  - Lipophilic
  - Hydrophilic