STU FCHPT

Selected wood chemical properties – bridge to technology

Radko Tiňo

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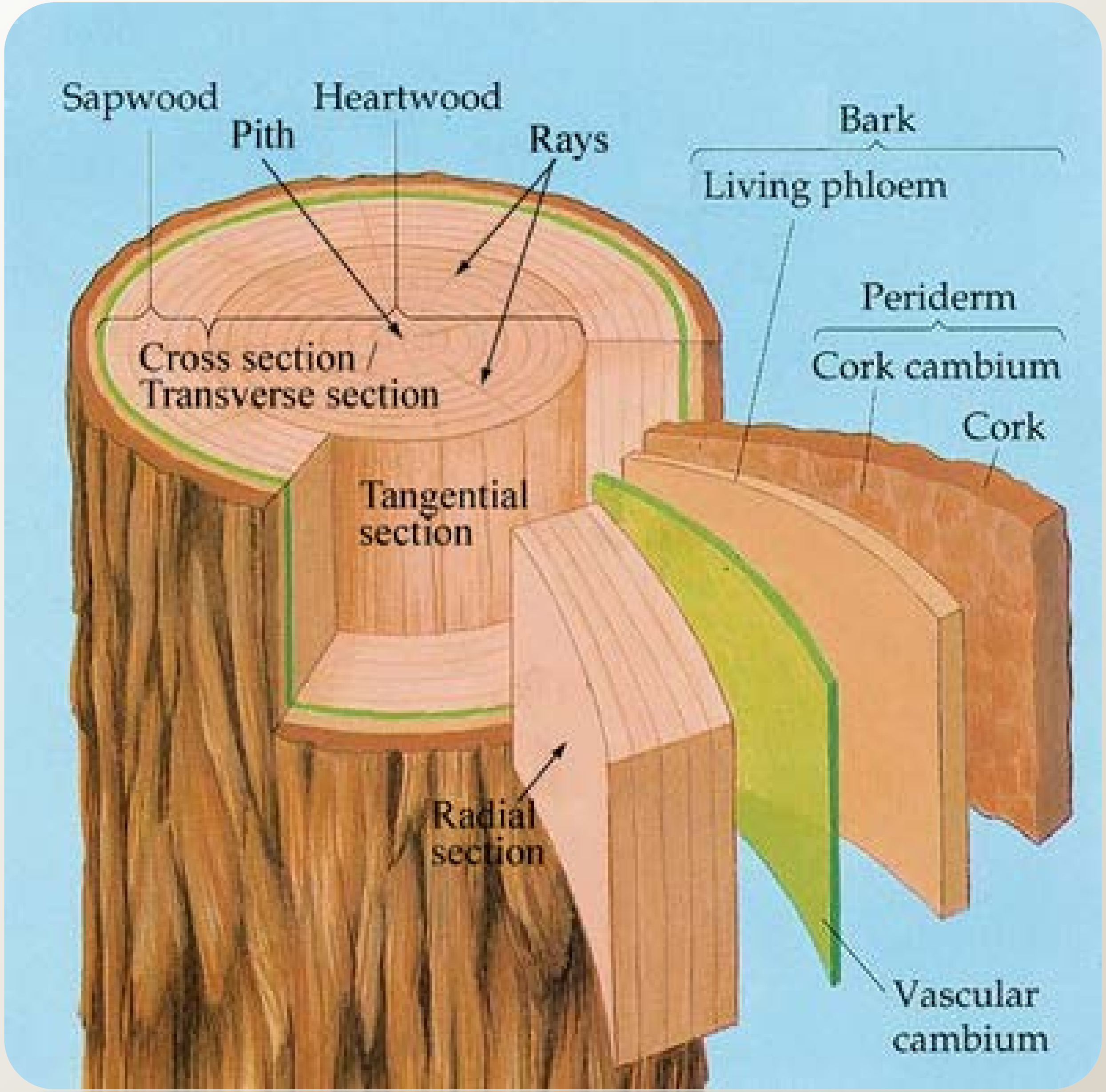
01

What is the wood?

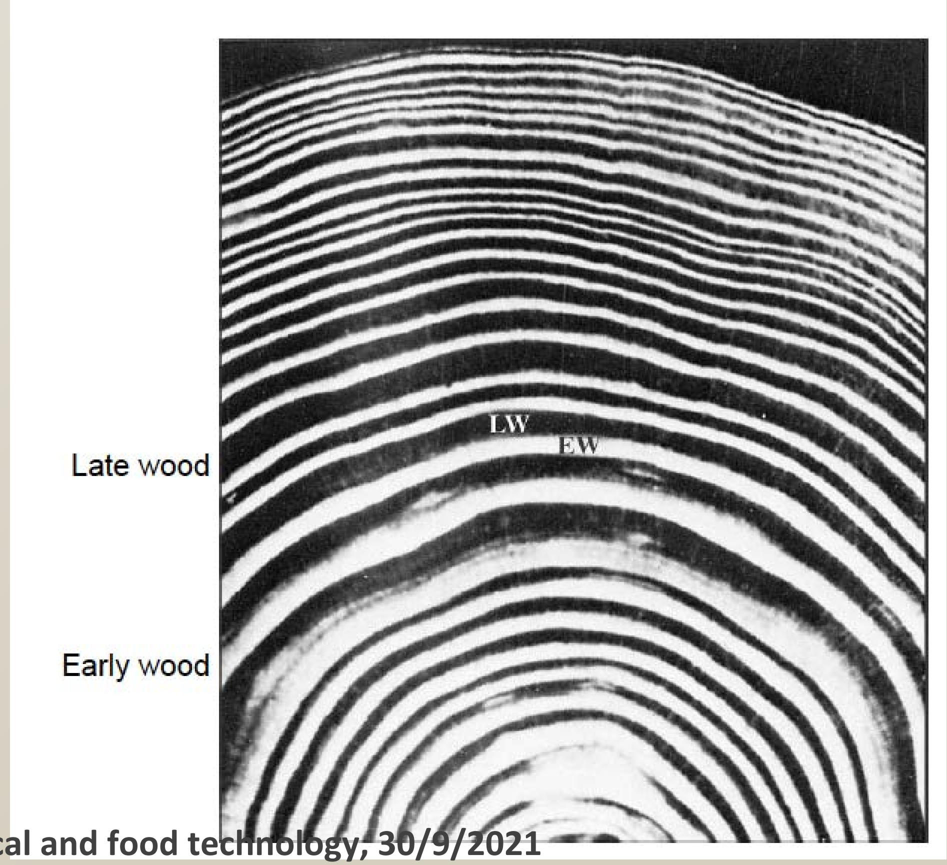
Wood is **complex** porous and fibrous structural **tissue** found in the stems and roots of trees and other **woody** plants.

It is an organic material, a **natural composite of cellulose fibers** (which are strong in tension) embedded in a **matrix of lignin** which resists compression.

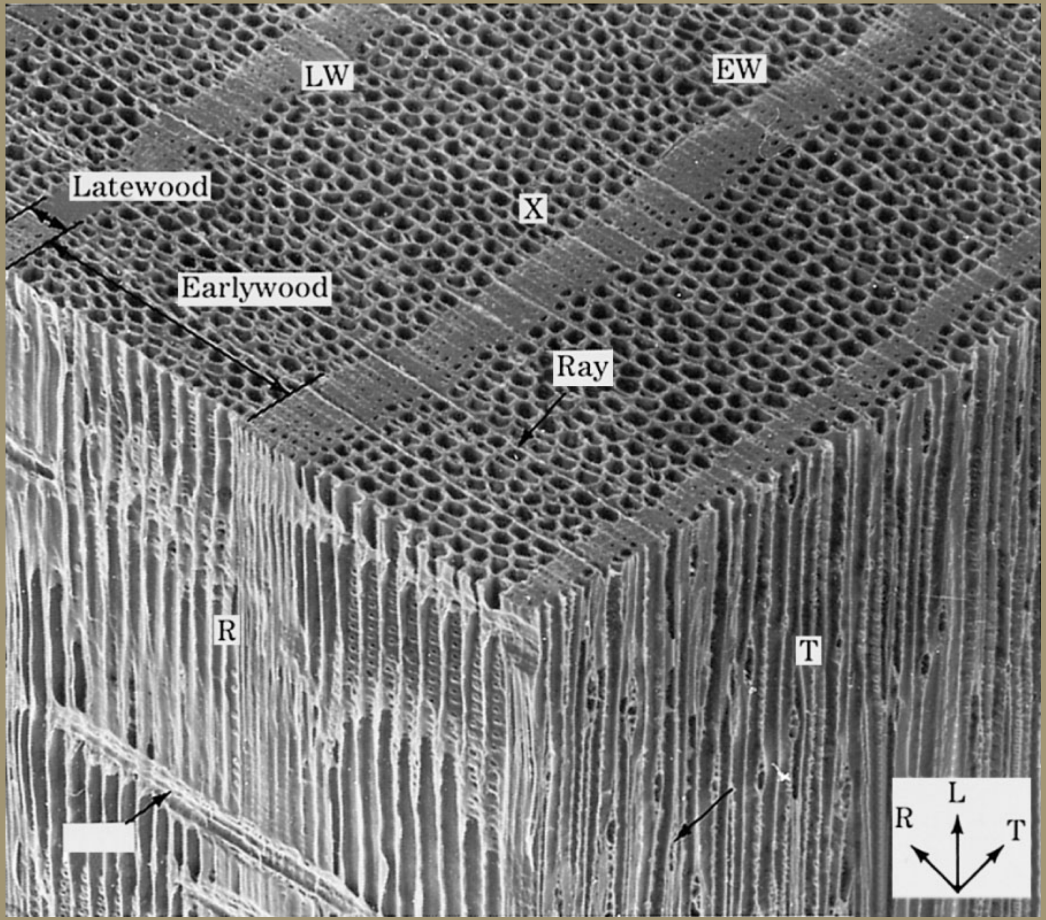
Wood has **extreme anisotropy** because **90 to 95%** of all the cells are **elongated and vertical** (i.e. *aligned parallel to the tree trunk*). The remaining 5 to 10% of cells are arranged in **radial directions**, with **no cells** at all aligned tangentially.



Three main sections
the heartwood, which is *physiologically inactive*,
the sapwood, where all conduction and storage occurs,
the bark, which *protects* the interior of the tree trunk.

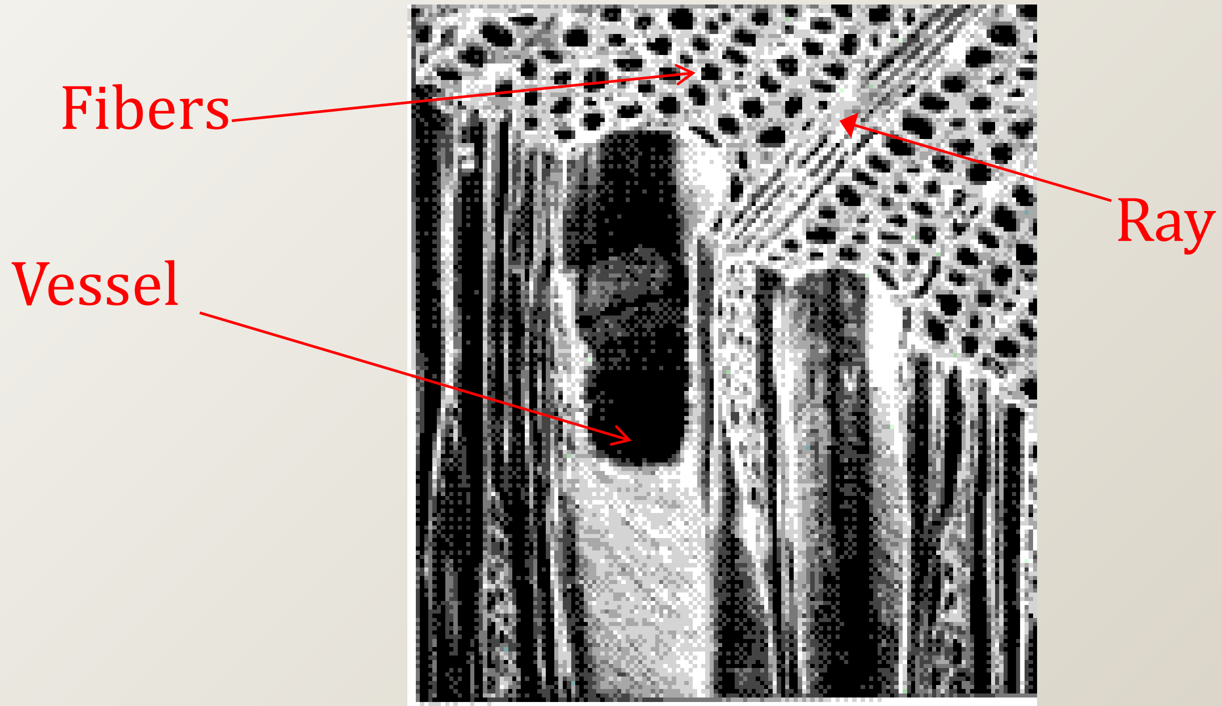


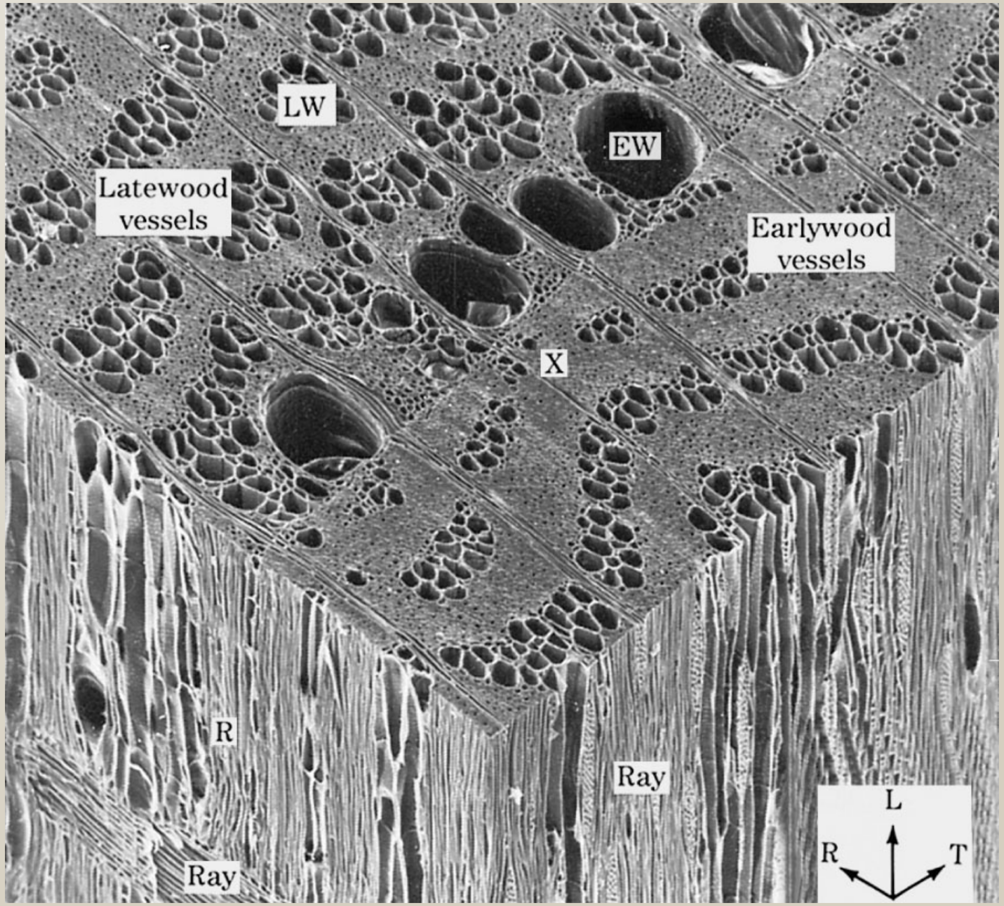
Softwoods consist **mainly** of long (3 to 5 mm) cells called **tracheids** which are about 20 to 80 x 10^{-6}m.

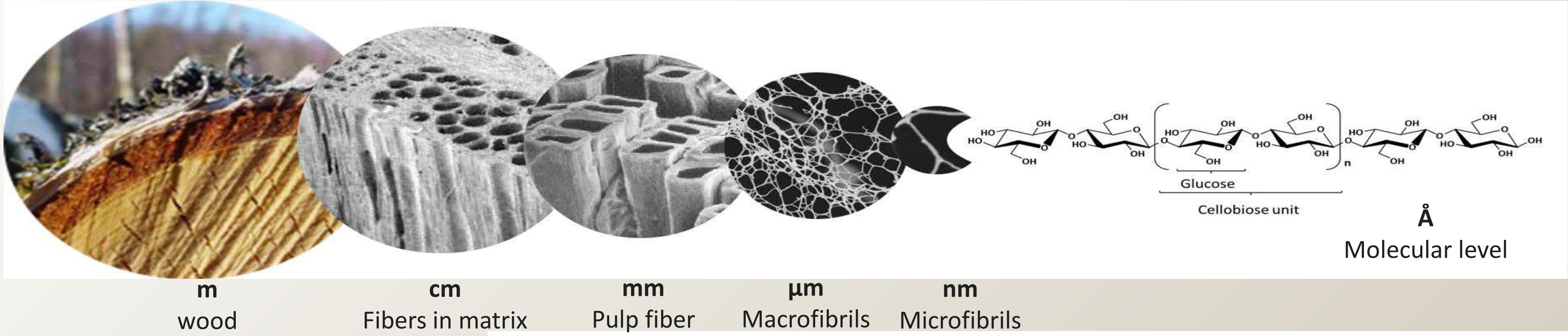


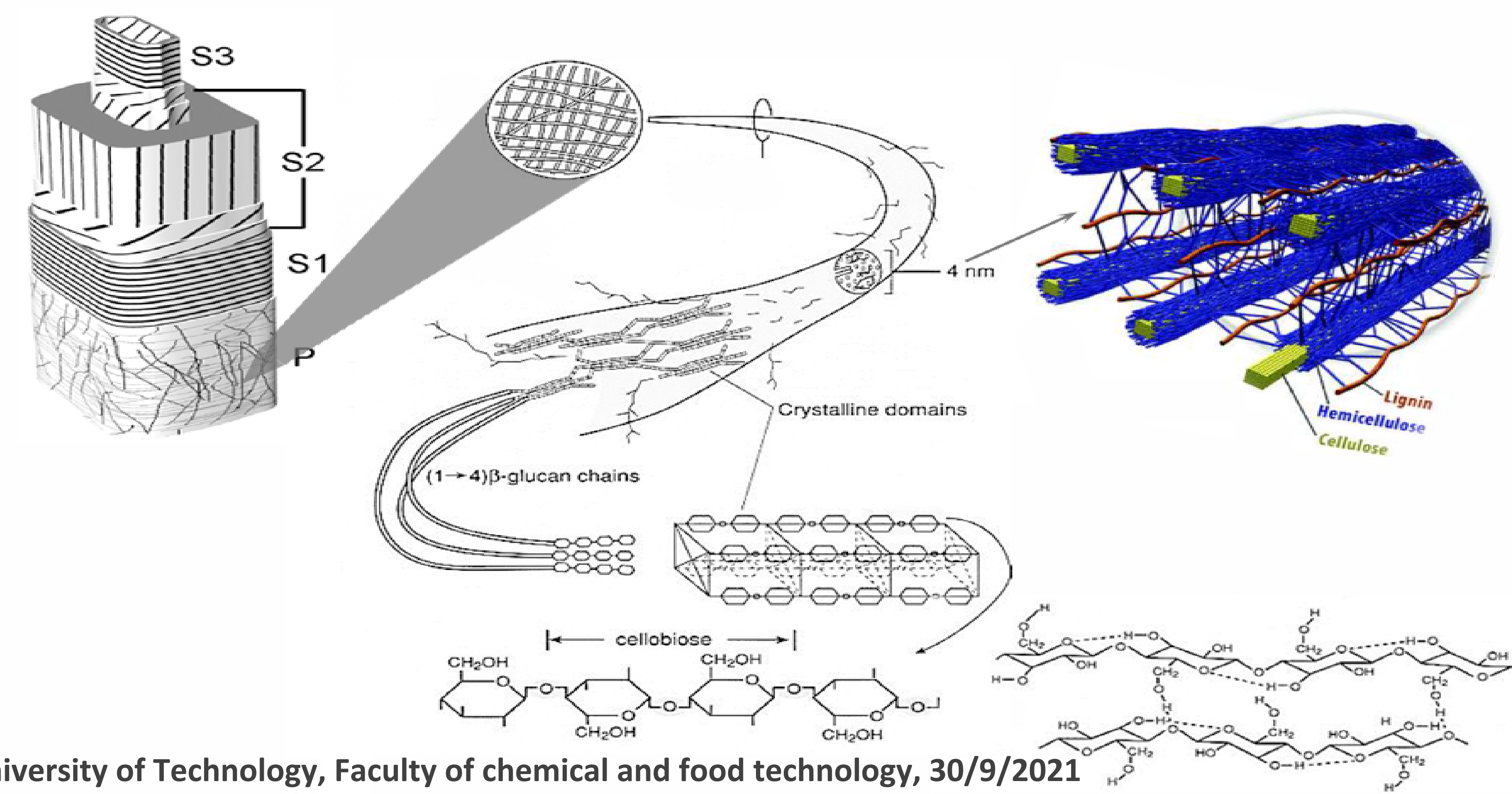
Hardwoods consist mainly of two kinds of cells:

– **Wood fibers** are elongated cells which are similar to tracheids except they are smaller, only 0.7 to 3 mm long and less than 20×10^{-6}m in diameter, and they do not serve for fluid transport in the living tree.
– **The vessel elements** do serve for fluid transport in the living tree, and they can have a wide range of sizes.



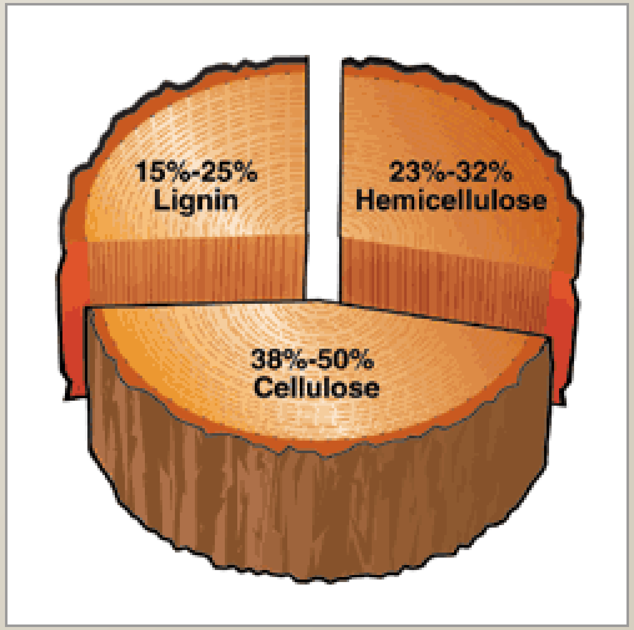



Glucose
Cellobiose unit
Å
Molecular level
m
wood
cm
Fibers in matrix
mm
Pulp fiber
µm
Macrofibrils
nm
Microfibrils


S3
S2
S1
P
4 nm
Crystalline domains
(1→4)β-glucan chains
cellobiose
Lignin
Hemicellulose
Cellulose

Classification of substances in wood

- Main components (90 -97%)
  - Saccharidic (70%)
    - Cellulose
    - hemicelluloses
  - Aromatic (25%) - lignin
- Accessoric components (3-10%) (extractives)
  - Inorganic (ash) (0,5%)
  - Organic – saccharides. Phenols, terpenes, acyclic acids, alcohols, proteins, etc.

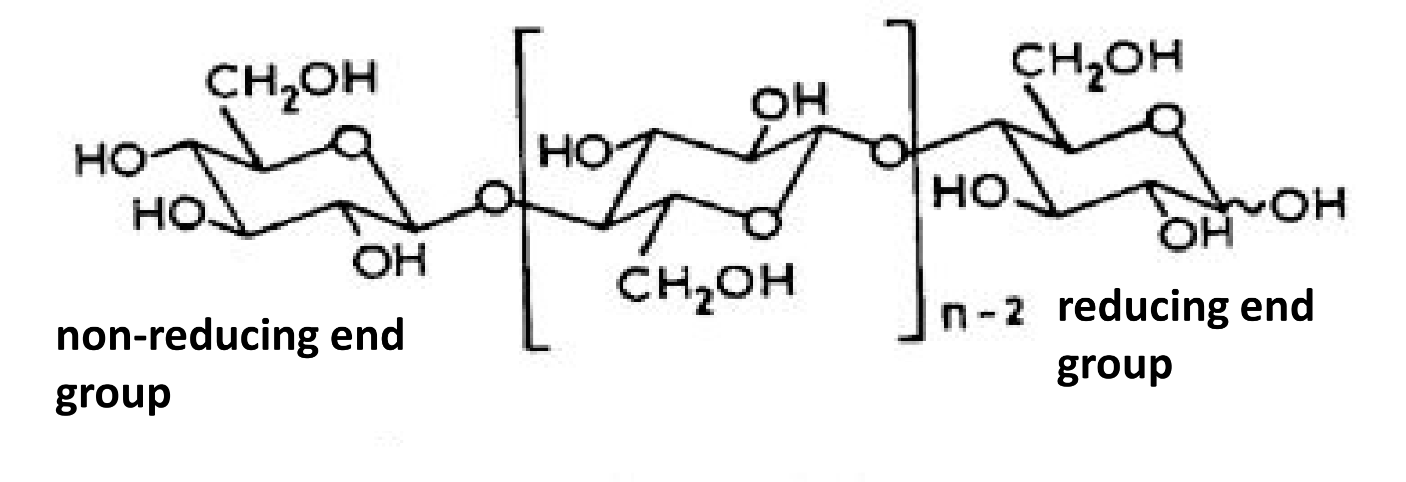


Chemical Constituents of Wood

The chemical composition of wood varies from species to species, but is approximately **50% carbon, 42% oxygen, 6% hydrogen, 1% nitrogen, and 1% other elements** (mainly *calcium, potassium, sodium, magnesium, iron, and manganese*) by weight.

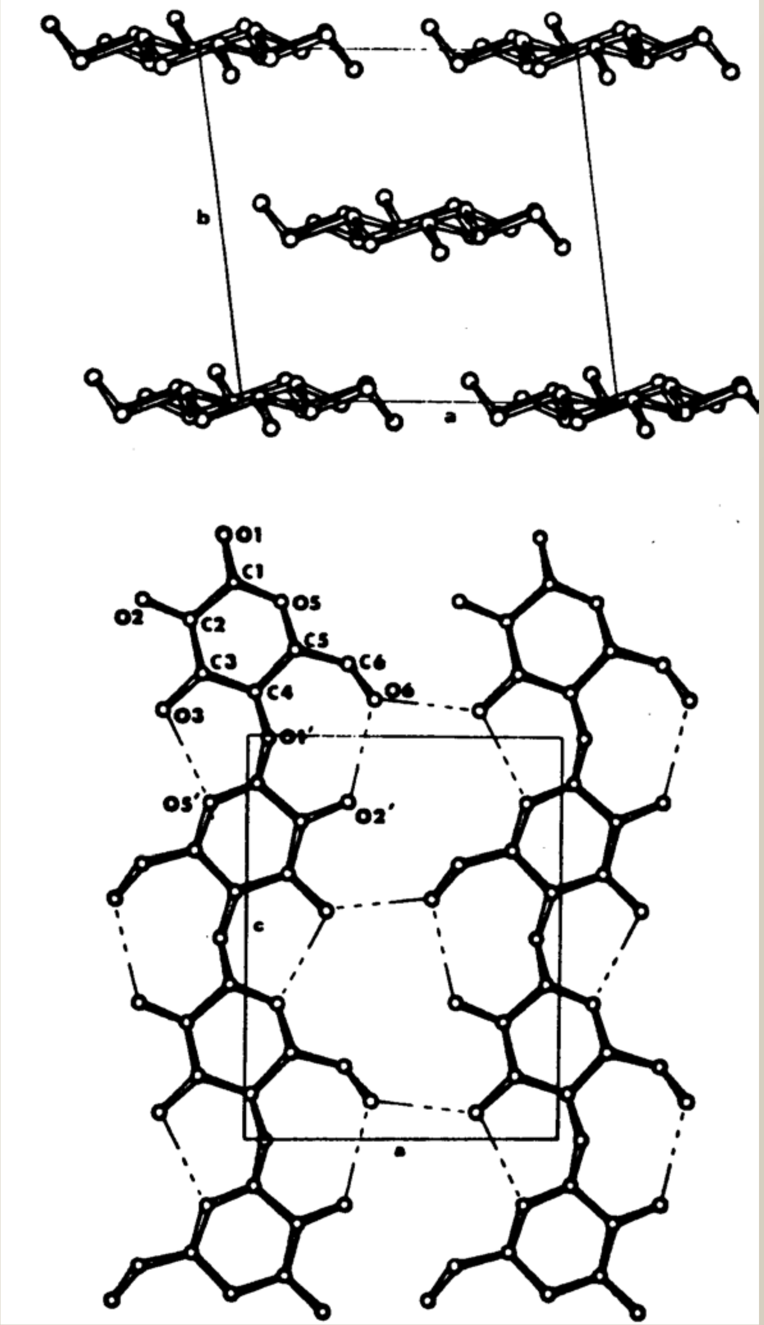
Wood also contains *sulfur, chlorine, silicon, phosphorus*, and other elements in small quantity.

Cellulose



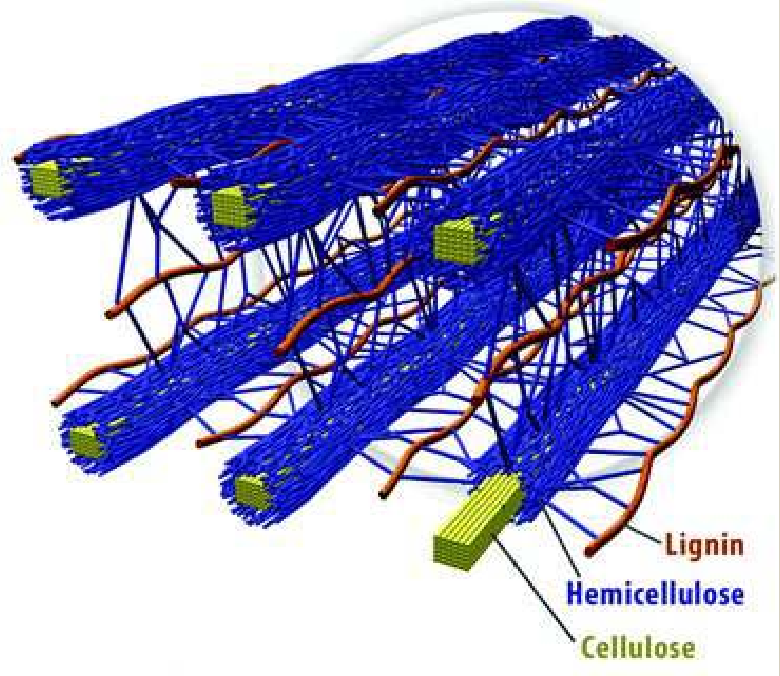
- linear homopolysaccharide
- Cellulose is a glucan polymer consisting of linear chains of 1,4-b -bonded anhydroglucose units. (*The notation 1,4-b describes the bond linkage and the configuration of the oxygen atom between adjacent glucose units.*)
- The number of sugar units in one molecular chain is referred to as the degree of polymerization (DP).
- A DP of 10,000 would mean a linear chain length of approximately 5 µm in wood.
- Cellulose in the primary wall has a lower DP and is thought to be polydisperse.

- Native cellulose is partially crystalline.
- The unit cell contains eight cellobiose moieties. The molecular chains pack in layers that are held together by weak van der Waals' forces
- The layers consist of parallel chains of **anhydroglucose units**, and the chains are held together by **intermolecular hydrogen bonds**. There are also intramolecular hydrogen bonds between the atoms of adjacent glucose residue
- This structure is called cellulose I.



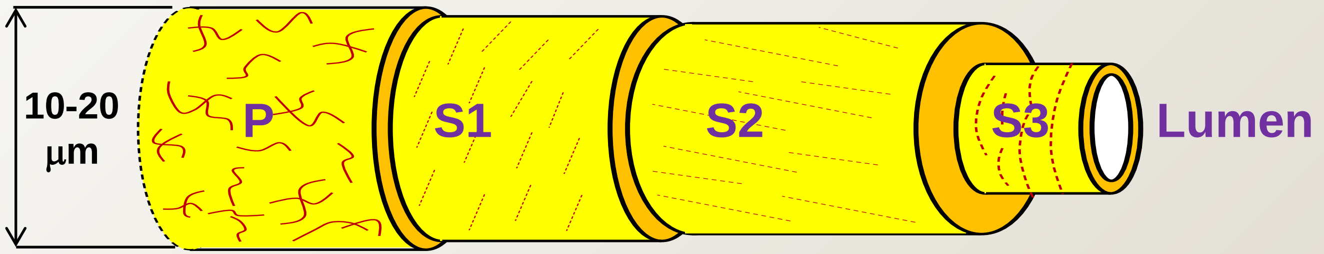
- Cellulose is **insoluble in most solvents** including strong alkali**.**

- **It is difficult to isolate from wood in pure form because it is intimately associated with the lignin and hemicelluloses.**

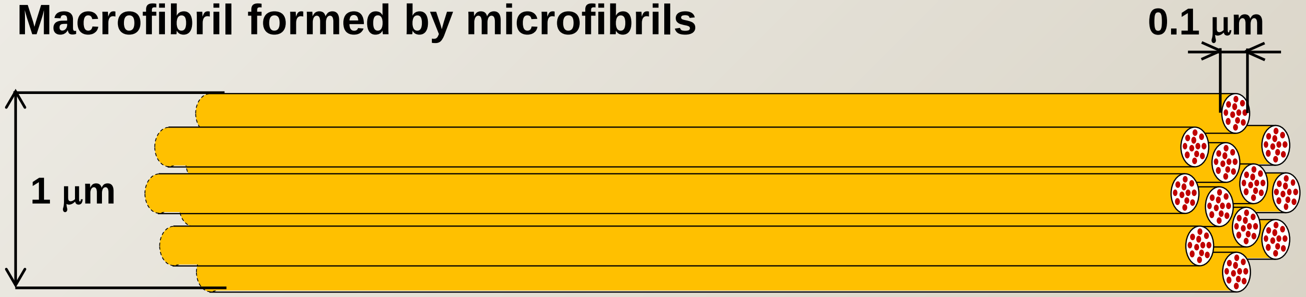


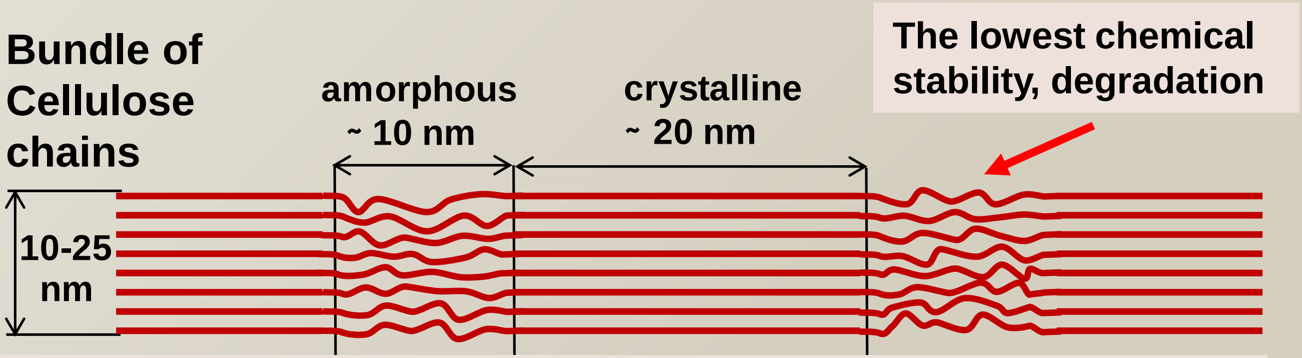
Dimensions of the hierarchical cellulose structure

Fiber wall sublayers: P – Primary, S1, S2, S3 – secondary



Macrofibril formed by microfibrils





Internal transport: reactants have to reach surface of cellulose chains (nanometric scale)

Chemical Constituents of Wood

Hemicelluloses constitutes about **20% in deciduous trees** but near **30% in conifers**. It is mainly five and six-carbon sugars that are linked in an irregular manner, in contrast to the cellulose.

Lignin is the third component at around **27% in coniferous** wood vs. **23% in deciduous trees**. Lignin confers the **hydrophobic properties** reflecting the fact that it is based on aromatic rings.

Aside from the „lignocellulose“, wood consists of a variety of **low molecular weight organic compounds**, called **extractives**.
The wood extractives are **fatty acids, resin acids, waxes** and **terpenes**.
For example, **resin** is exuded by **conifers** as **protection from insects**.

Hemicelluloses

- linear polysaccharides partially branched, containing short side chains

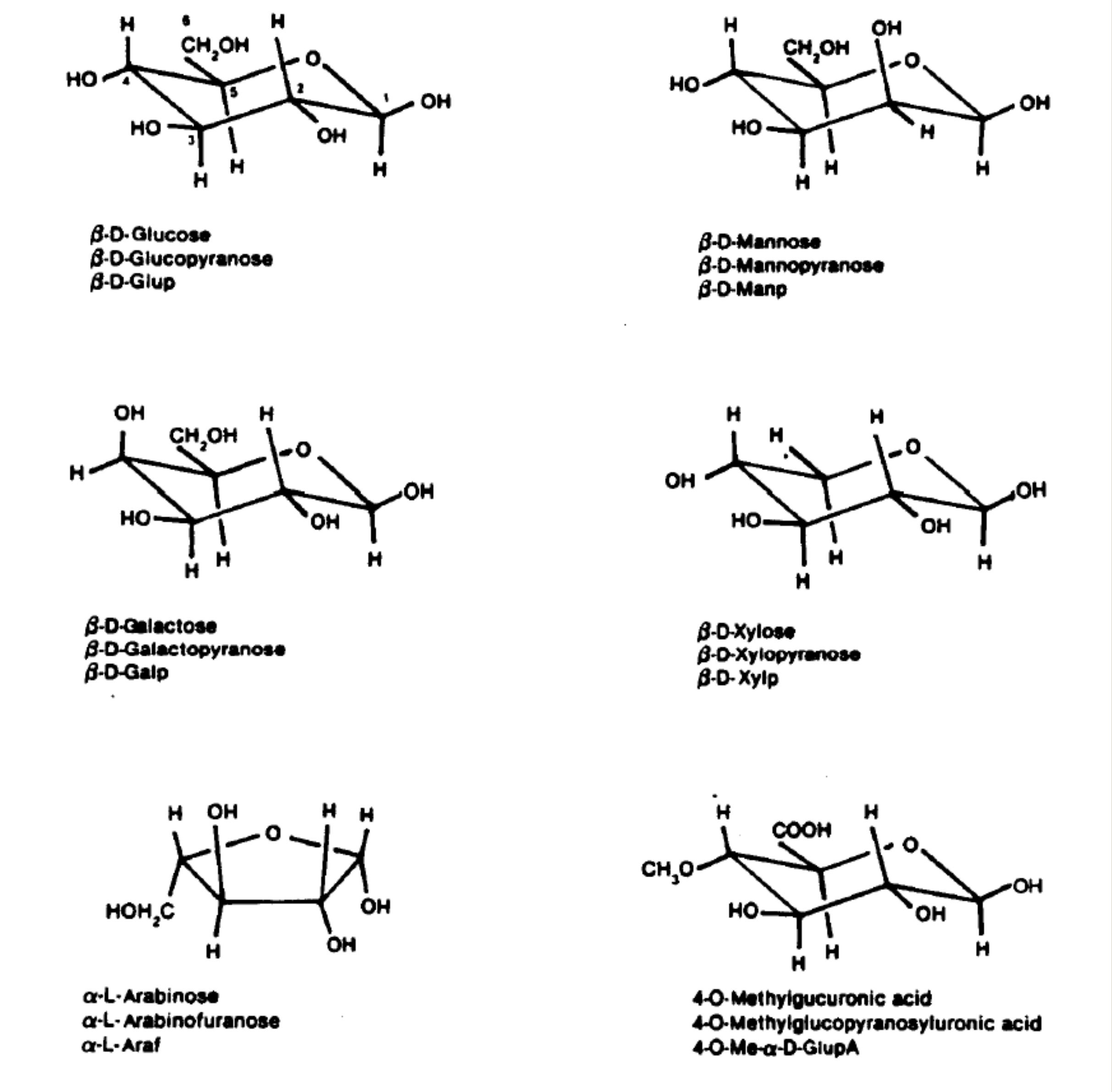
- mixtures of polysaccharides synthesized in wood almost entirely from glucose, mannose, galactose, xylose, arabinose, 4-*O* methylglucuronic acid, and galacturonic acid residues.

- accompanying cellulose in layers of the cell wall

- They are intimately associated with cellulose and appear to contribute as a structural component in the plant.

- Some hemicelluloses are present in abnormally large amounts when the plant is under stress; e.g., compression wood has a higher than normal galactose content as well as a higher lignin content.

- Hemicelluloses are soluble in alkali and easily hydrolyzed by acids.



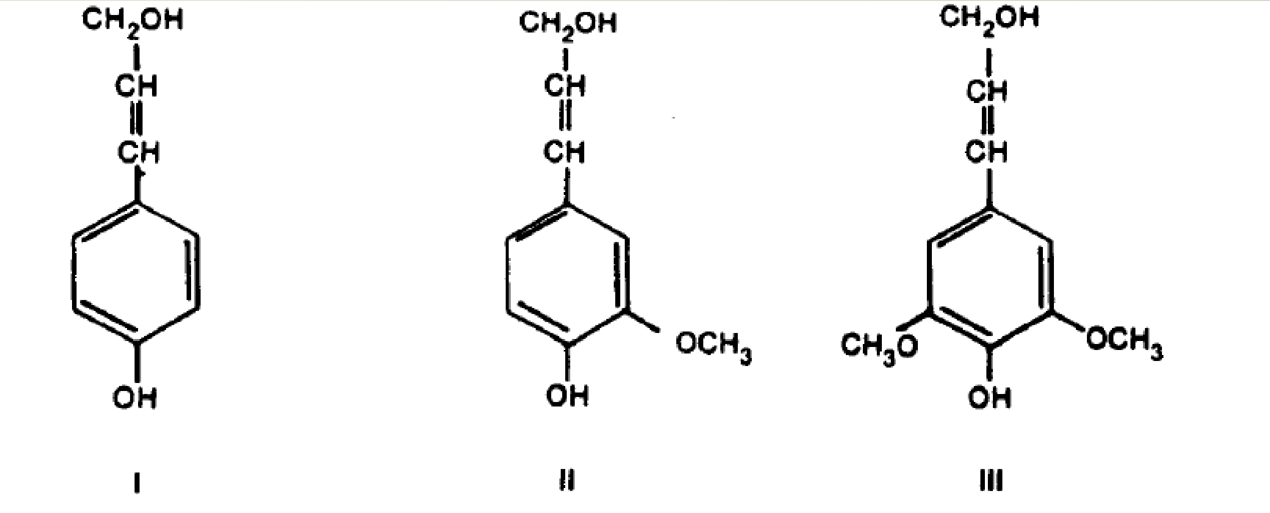
Hemicellulose Type	Occurrence	Amount (% of wood)	Composition			Solubility[a]	$\overline{DP}_n$[b]
			Units	Molar Ratios	Linkage		
Galactoglucomannan	Softwood	5–8	β-D-Man*p*	3	1 → 4	Alkali, water*	100
			β-D-Glu*p*	1	1 → 4		
			α-D-Gal*p*	1	1 → 6		
			Acetyl				
(Galacto)Glucomannan	Softwood	10–15	β-D-Man*p*	4	1 → 4	Alkaline borate	100
			β-D-Glu*p*	1	1 → 4		
			α-D-Gal*p*	0.1	1 → 6		
			Acetyl	1			
Arabinoglucuronoxylan	Softwood	7–10	β-D-Xyl*p*	10	1 → 4	Alkali, dimethyl sulfoxide,* water*	100
			4-*O*-Me-α-D-Glu*p*A	2	1 → 2		
			α-L-Ara*f*	1.3	1 → 3		
Arabinogalactan	Larch wood	5–35	β-D-Gal*p*	6	1 → 3, 1 → 6	Water	200
			α-L-Ara*f*	2/3	1 → 6		
			β-L-Ara*p*	1/3	1 → 3		
			β-D-Glu*p*A	Little	1 → 6		
Glucuronoxylan	Hardwood	15–30	β-D-Xyl*p*	10	1 → 4	Alkali, dimethyl sulfoxide*	200
			4-*O*-Me-α-D-Glu*p*A	1	1 → 2		
			Acetyl	7			
Glucomannan	Hardwood	2–5	β-D-Man*p*	1–2	1 → 4	Alkaline borate	200
			β-D-Glu*p*		1 → 4		

[a] The asterisk represents a partial solubility.
[b] $\overline{DP}_n$ is the number average degree of polymerization, usually obtained by osmometry.

Lignin

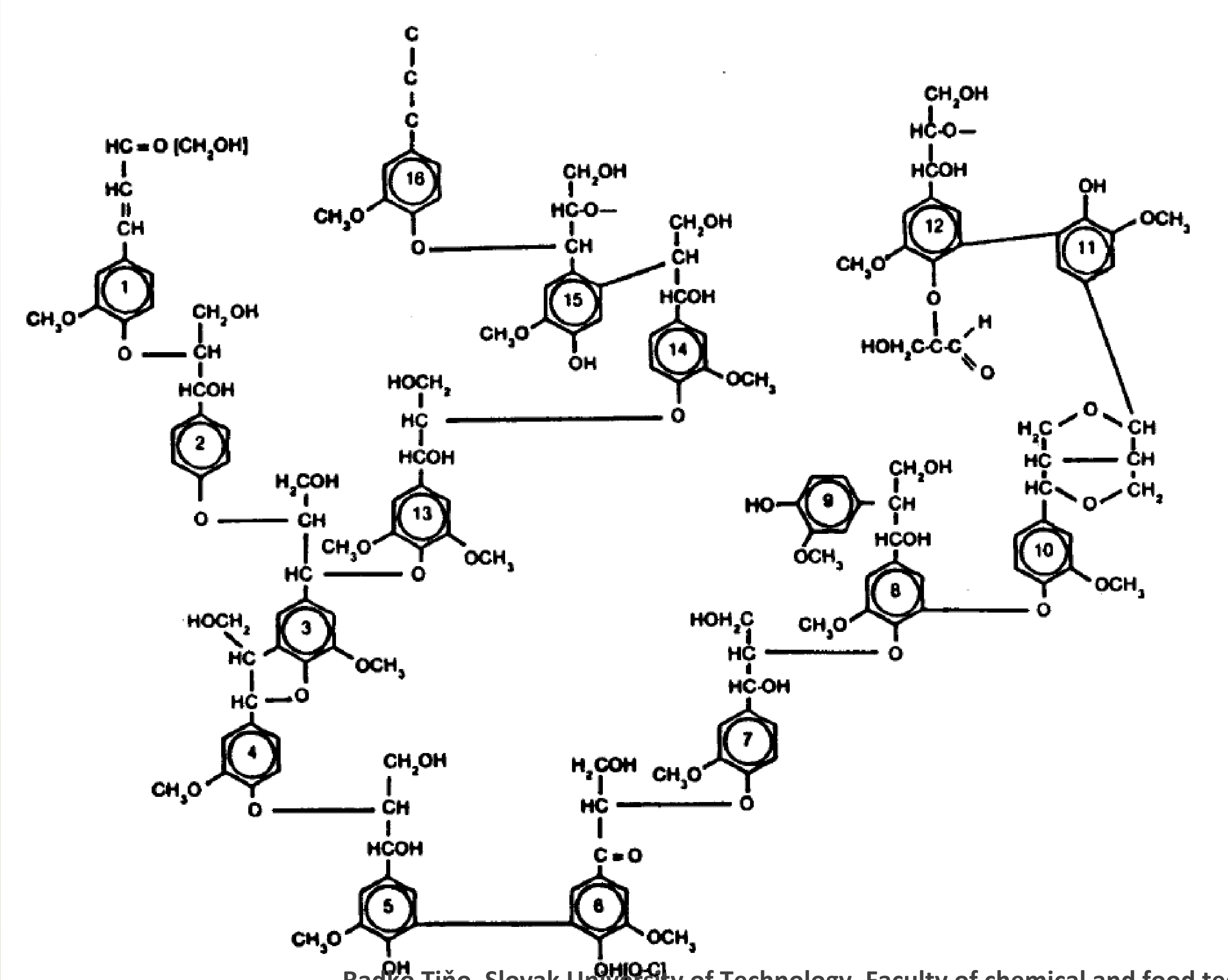
- phenolic substance consisting of an irregular array of variously bonded hydroxy- and methoxy-substituted phenylpropane units.
- I is a minor precursor of softwood and hardwood lignins;
- II is the predominant precursor of softwood lignin;
- II and III are both precursors of hardwood lignin

The precursors of lignin biosynthesis



p-coumaryl alcohol   coniferyl alcohol   sinapyl alcohol

Partial structure of softwood lignin

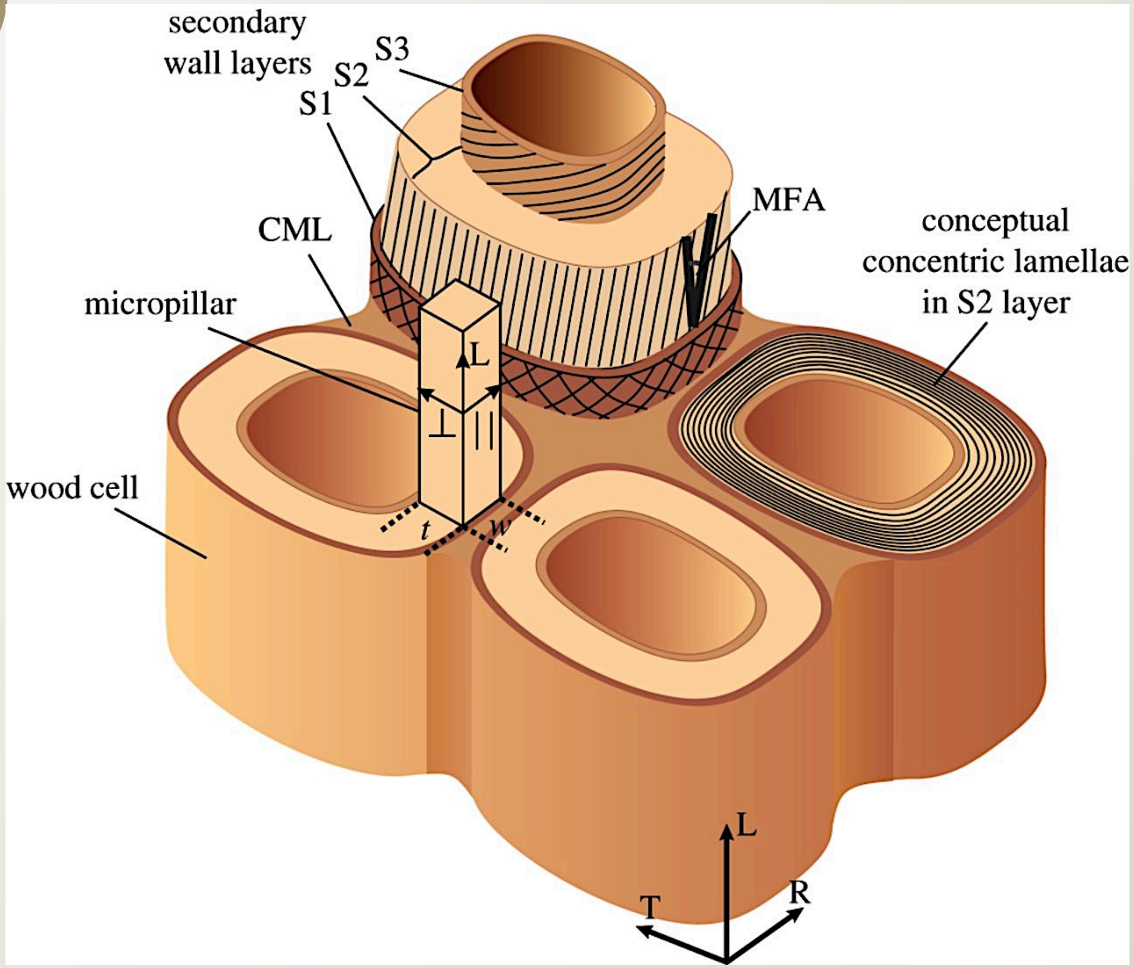


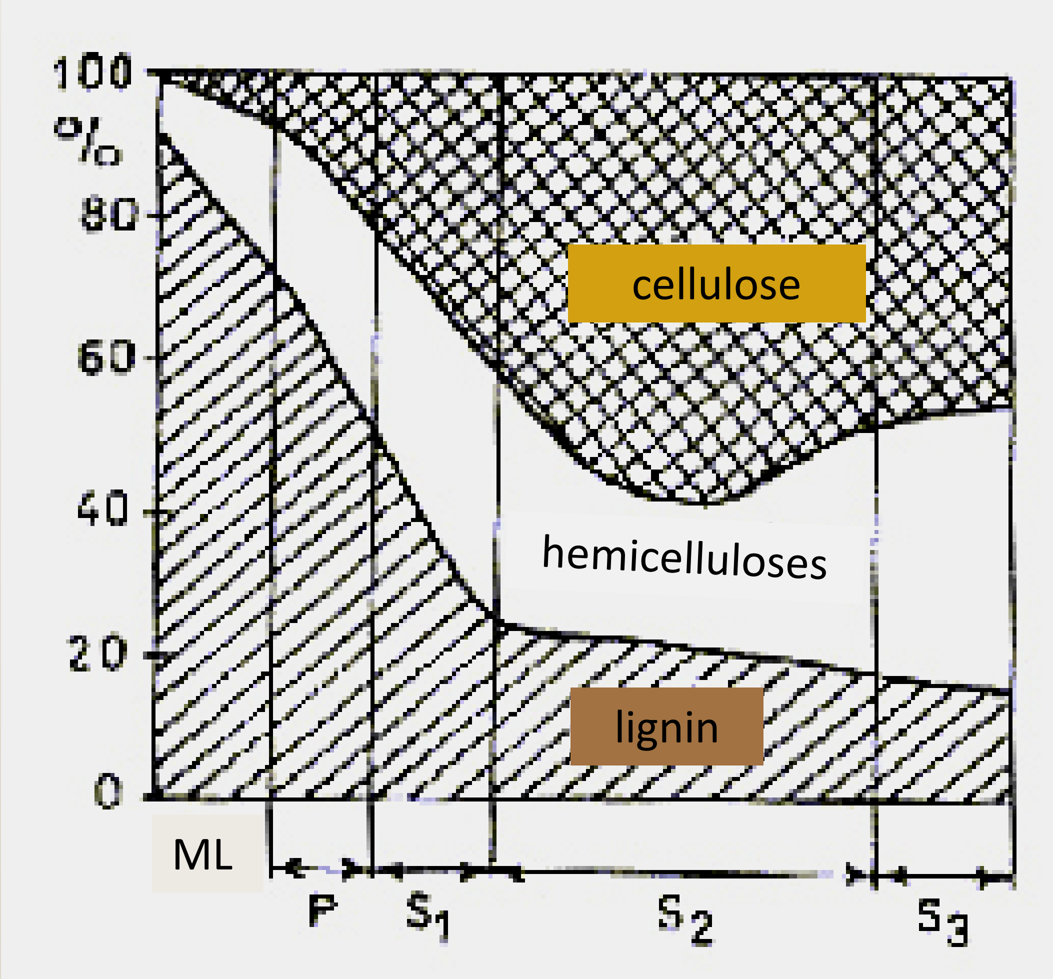
A structure proposed for **hardwood lignin** *(Fagus silvatica* L.) is similar, except that there are three times as many syringylpropane units as guaiacylpropane units

The ratio of syringyl to guaiacyl moieties is often obtained by **measuring the relative amounts** of **syringaldehyde** (3, 5-dimethoxy-4-hy droxybenzaldehyde) and **vanillin** (4-hydroxy-3-methoxybenzaldehyde) generated as products of nitrobenzene oxidation of lignin

Methoxyl content is used to characterize lignins. Methoxyl analysis of spruce (Picea abies (L.)) milled wood lignin indicates a composition $C_9H_{7.92}O_{2.40}(OCH_3)_{0.92}$. Beech (Fagus silvatica L.) milled wood lignin has a composition $C_9H_{7.49}O_{2.53}(OCH_3)_{1.39}$

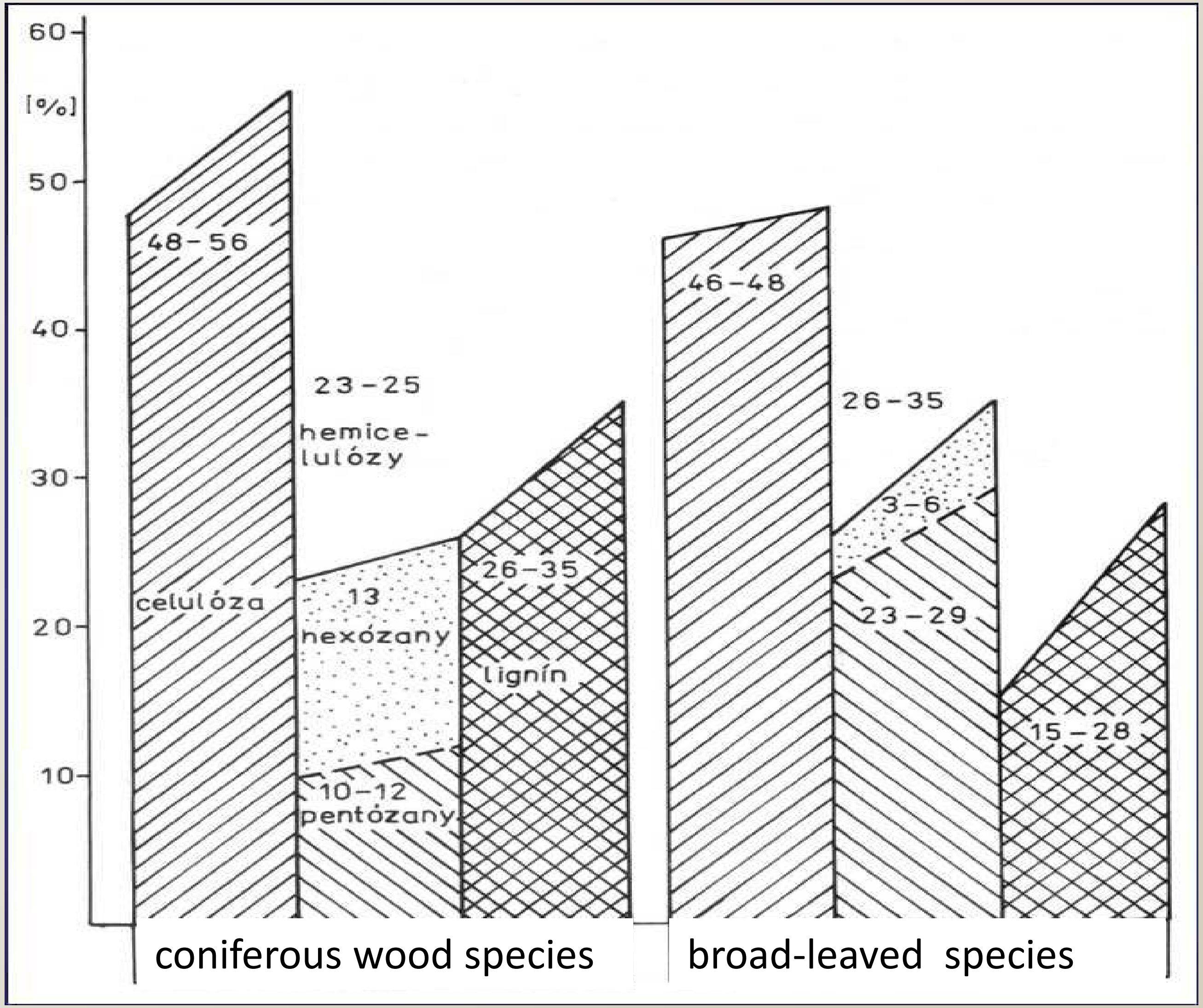
The tubular cell wall has a layered structure:





The **open space in dry wood** is approximately **50%,** but **can be** as high as **92% in balsa wood**.

Comparison of main compounds in wood



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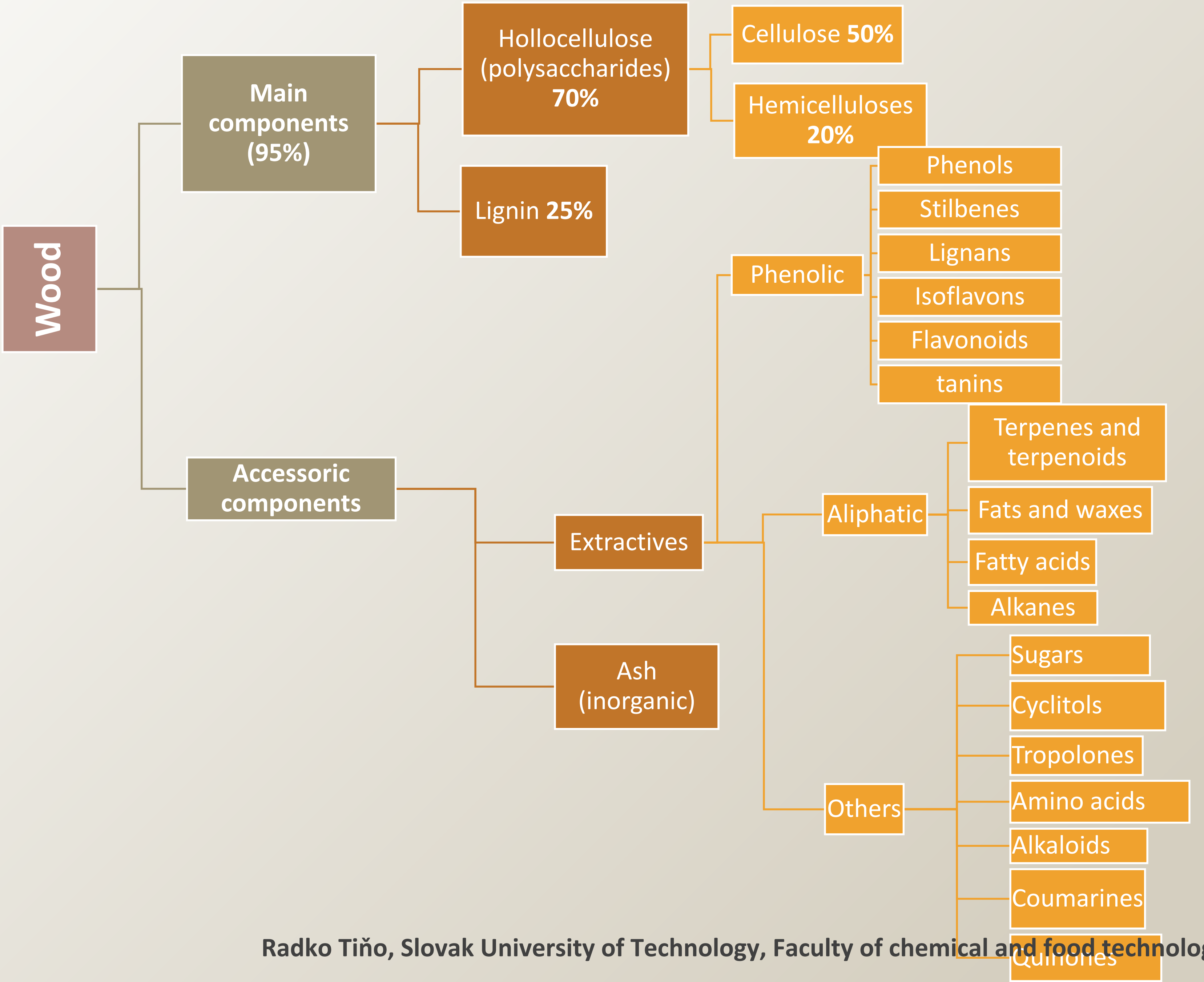

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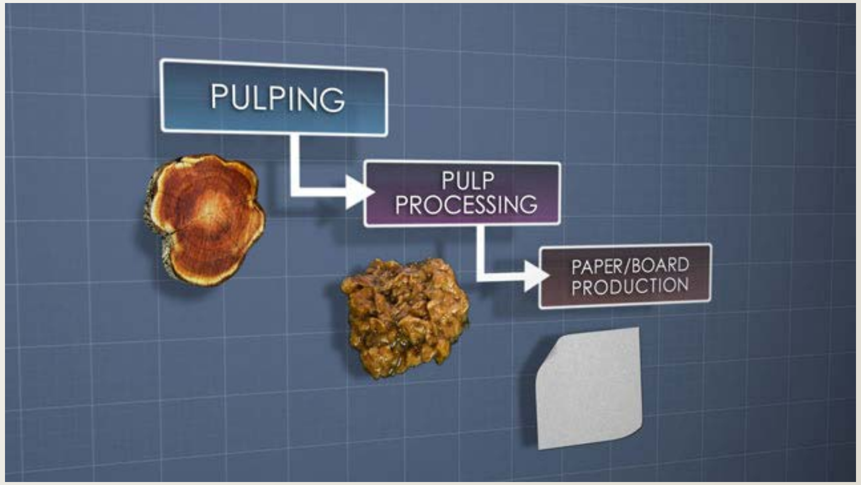
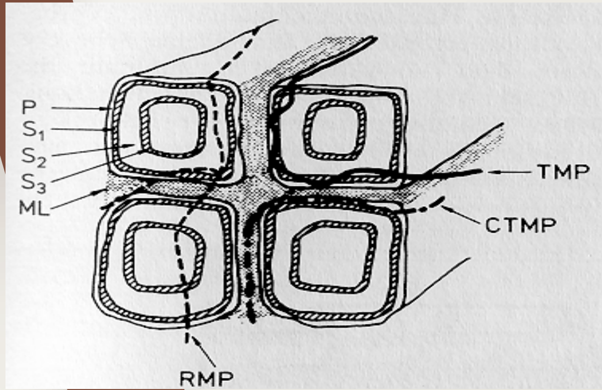
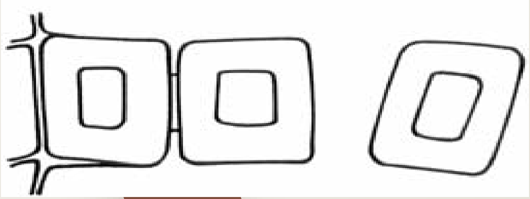
Chemical composition of main wood species in Central Europe

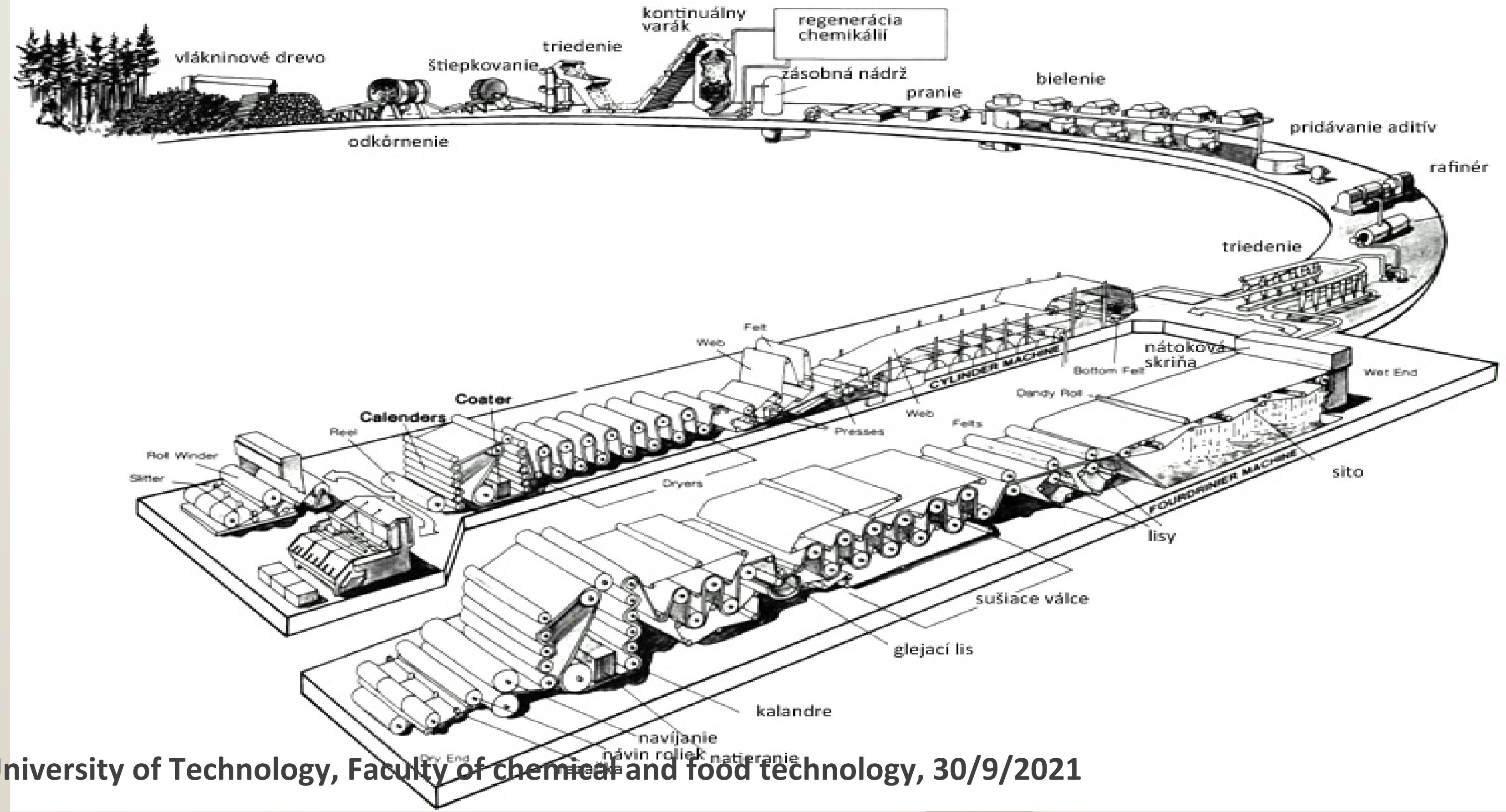
Component	Spruce european *(Picea excelsa)*	Pine common /Scots pine *(Pinus silvestris)*	Beech copper *(Fagus silvatica)*	Common Oak *(Quercus robur)*
ash	0,8	0,4	1,2	0,6
lignin	26,9	26,6	20,9	22,6
α-cellulose	45,6	43,2	39,2	46,3
hemicelluloses	27,6	28,0	35,3	36,7
- manose	16,0	12,5	1,5	-
- xylose	9,0	13,0	28,0	-
extractives	1-4,5	3-5	4,7	2,3-5,6

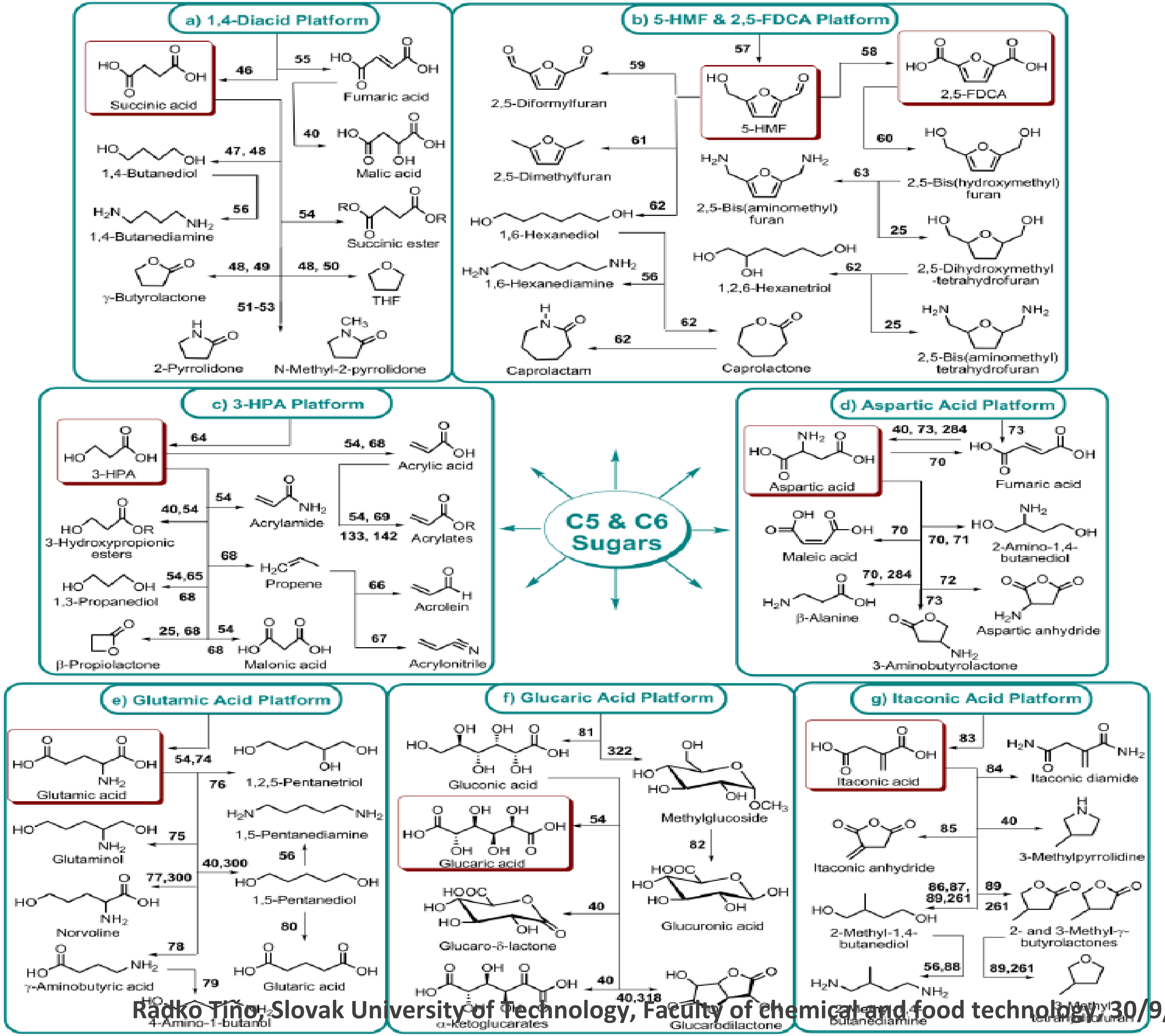
Pulping and papermaking

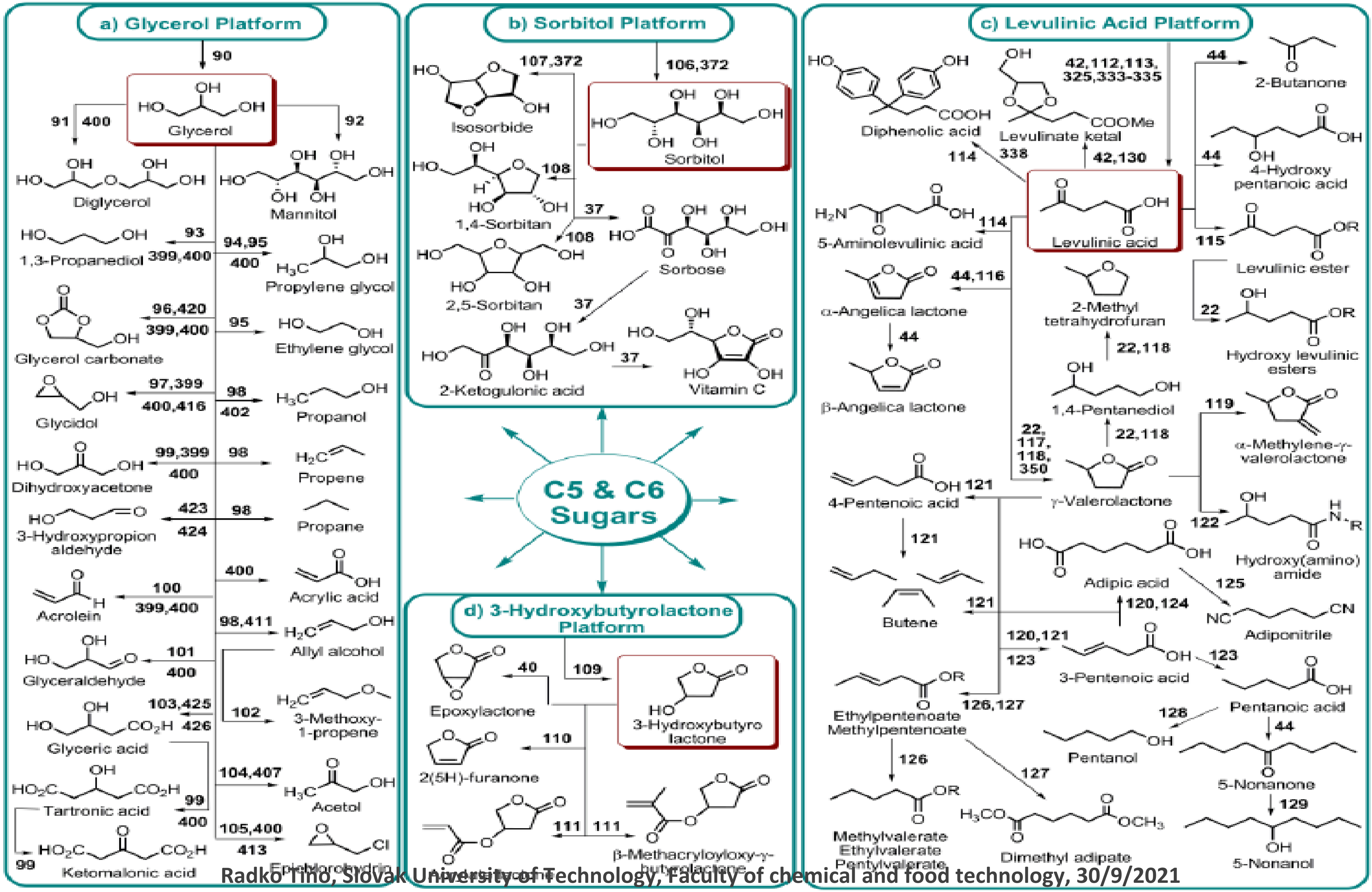









C5 & C6 Sugars
a) 1,4-Diacid Platform
Succinic acid
Fumaric acid
Malic acid
1,4-Butanediol
1,4-Butanediamine
Succinic ester
γ-Butyrolactone
THF
2-Pyrrolidone
N-Methyl-2-pyrrolidone
b) 5-HMF & 2,5-FDCA Platform
5-HMF
2,5-FDCA
2,5-Diformylfuran
2,5-Dimethylfuran
1,6-Hexanediol
1,6-Hexanediamine
Caprolactam
Caprolactone
2,5-Bis(aminomethyl) furan
2,5-Bis(hydroxymethyl) furan
2,5-Dihydroxymethyl -tetrahydrofuran
1,2,6-Hexanetriol
2,5-Bis(aminomethyl) tetrahydrofuran
c) 3-HPA Platform
3-HPA
Acrylic acid
Acrylamide
Acrylates
3-Hydroxypropionic esters
Propene
Acrolein
1,3-Propanediol
β-Propiolactone
Malonic acid
Acrylonitrile
d) Aspartic Acid Platform
Aspartic acid
Fumaric acid
Maleic acid
2-Amino-1,4-butanediol
β-Alanine
Aspartic anhydride
3-Aminobutyrolactone
e) Glutamic Acid Platform
Glutamic acid
1,2,5-Pentanetriol
1,5-Pentanediamine
Glutaminol
1,5-Pentanediol
Norvoline
γ-Aminobutyric acid
Glutaric acid
4-Amino-1-butanol
f) Glucaric Acid Platform
Gluconic acid
Glucaric acid
Methylglucoside
Glucuronic acid
Glucaro-δ-lactone
α-Ketoglucarates
Glucarodilactone
g) Itaconic Acid Platform
Itaconic acid
Itaconic diamide
Itaconic anhydride
3-Methylpyrrolidine
2-Methyl-1,4-butanediol
2- and 3-Methyl-γ-butyrolactones
butanediamine



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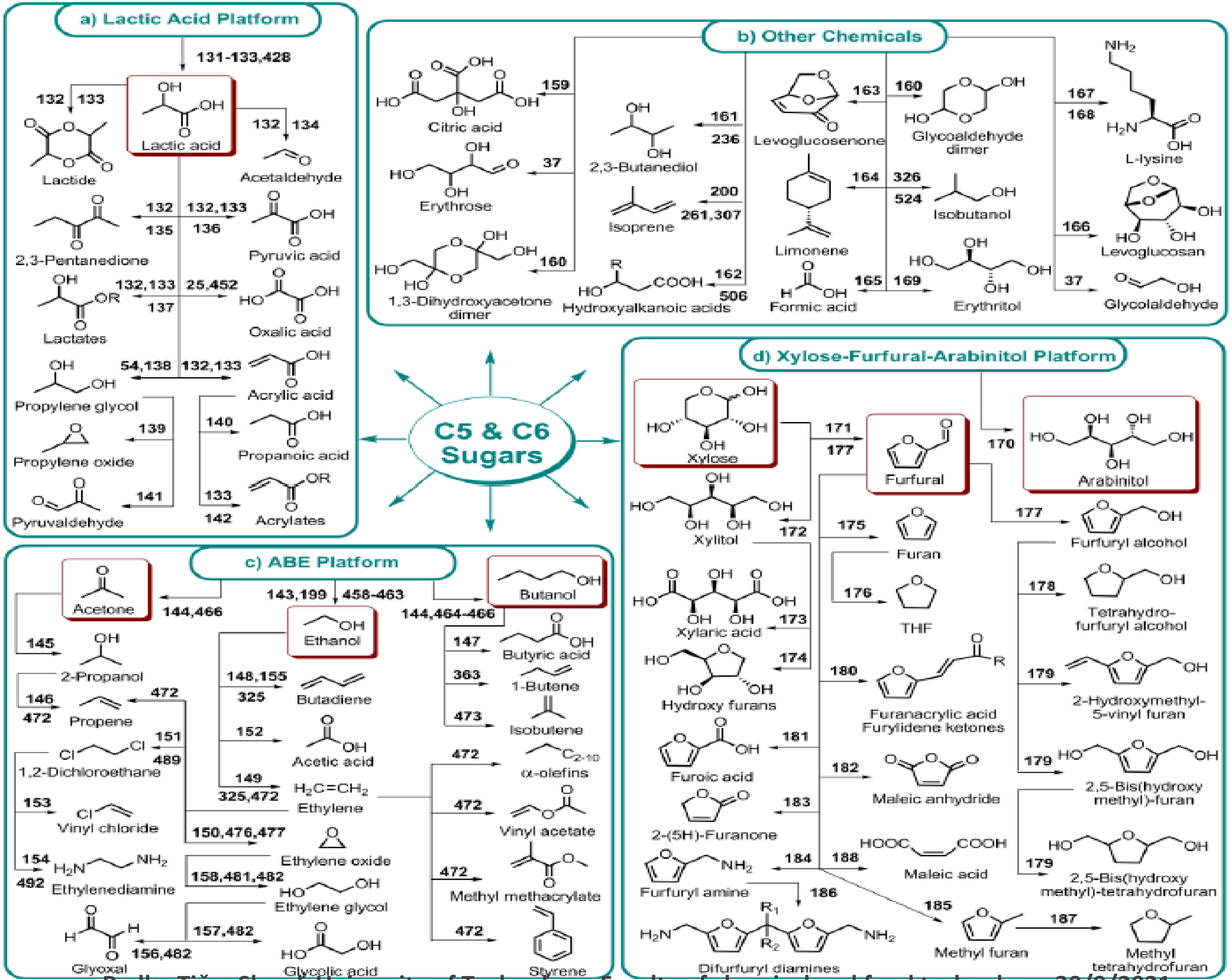

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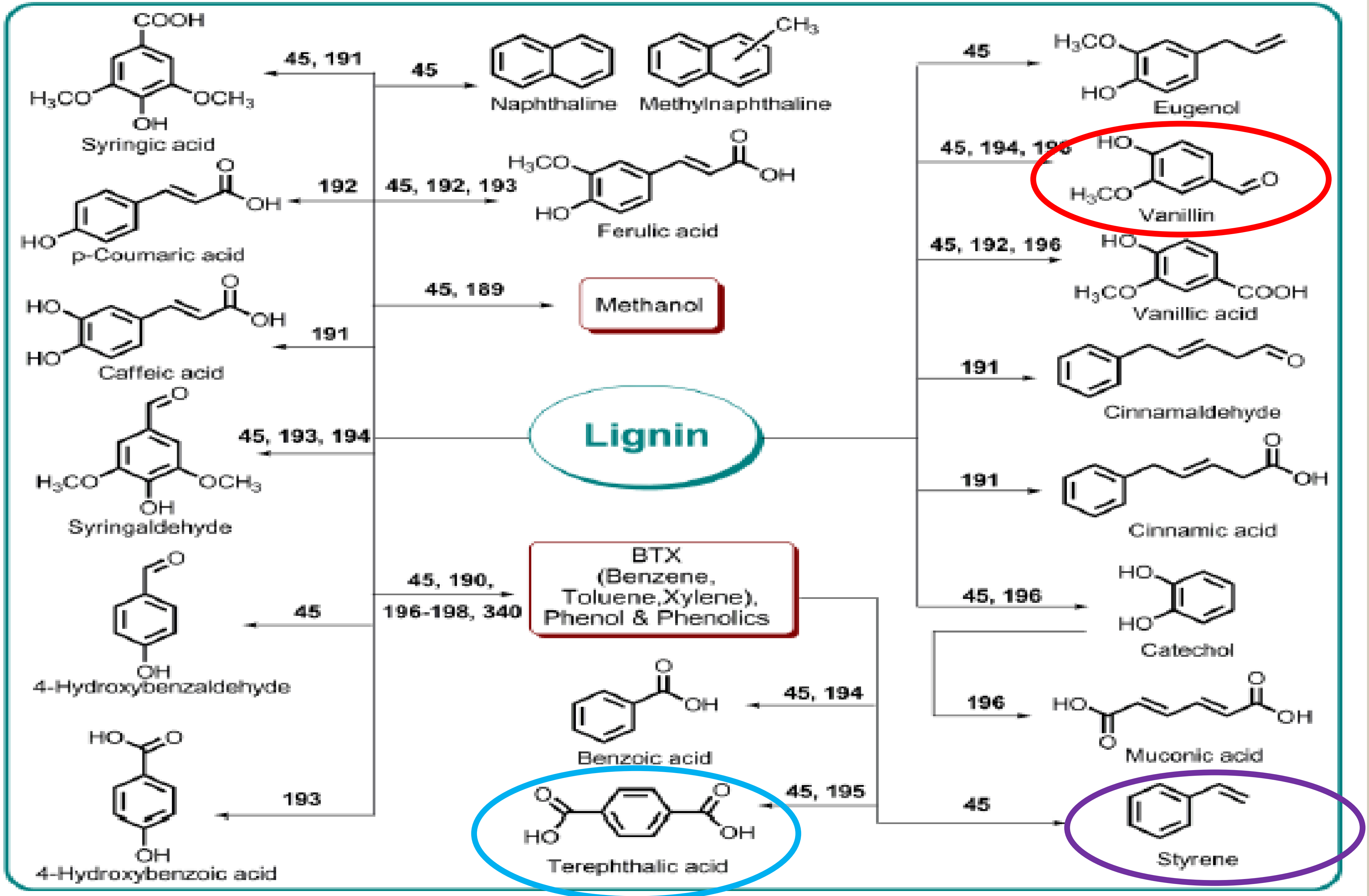

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Wood and water

Water is a **natural constituent** of all parts of a living tree.

In the xylem portion, water (moisture) commonly makes up over half the total weight.

Properties of wood depends on the water content of the wood:

- dimensions
- strength
- thermal conductivity
- resistance to fungi and molds
- electrical resistance
- dielectric properties

Wood and water

The mass of water in a **freshly felled tree** is **60 to 200% of the dry mass of the tree**.

In **dried out timber** there is only roughly **10 weight percent water content**.

However timbers tend to **achieve equilibrium with the surrounding air**, settling to a moisture content of **22 to 23% in moist, water-saturated air**.

Location of water in wood

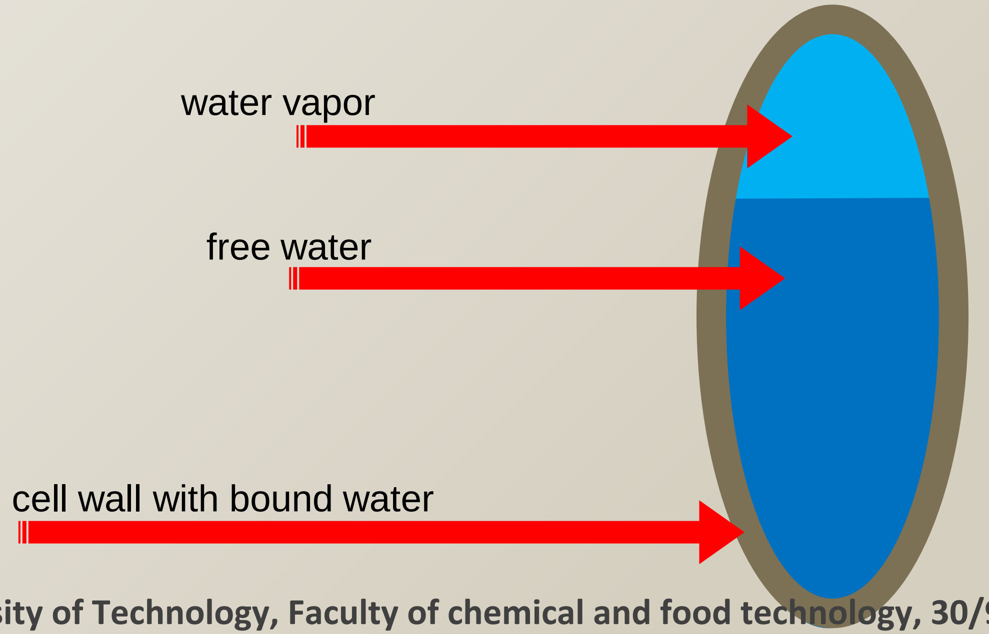
Location

In the cell walls – **bound water**

Water can stays in the cell walls at any moisture content level.

In the cell lumens – **free water**

Water stays in the cell lumens only when the wood is saturated, in other words, when the moisture content of wood is above the fiber saturation point (FSP).



Nature of water in wood

Free water

stayed in the cell lumens

held by the force of surface tension

easy to remove, just like the water in a pool

Bound water

stayed in the cell walls

held by adsorption force through H-bond

difficult to remove

H-bond force increases as MC decreases

Conception of absorption and adsorption

Absorption: results from surface tension forces.

Adsorption: involves the attraction of water molecules to hydrogen bonding sites.

Wood is hygroscopic.

- This means the **attraction between dry wood and water** is so **strong** it is impossible to prevent moisture gain.
- Water easily binds with the cellulose fibers (microfibrils) in the cell wall
- As wet wood dries**, free water leaves the lumens** (cell cavities) first. *Free water resembles liquid in a bucket. When you dump water out of a bucket, the bucket does not change shape. Similarly, wood does not shrink as it loses free water from the lumen.*
- After all the free water is gone and only bound water remains, the cell has reached its fiber saturation point (fsp).

Fiber saturation point

Definition

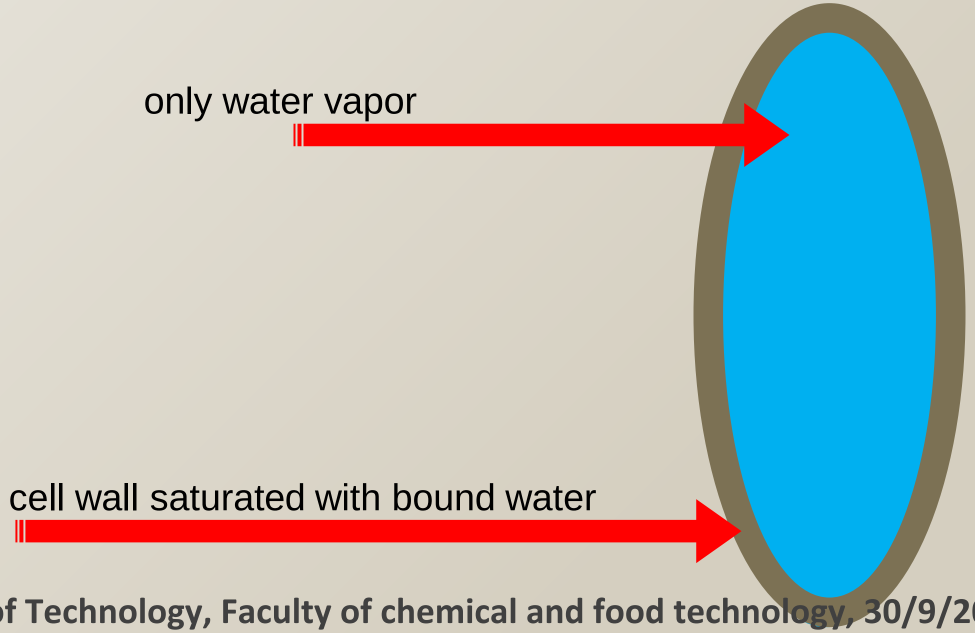
The point at which all the liquid water in the lumen has been removed but the cell wall is still saturated is termed the **fiber saturation point** (FSP).

Implication

This is a critical point, since below this point almost all properties of wood are altered by changes in moisture content.

Ranges

MC = 28-35%, usually take it as 30%.

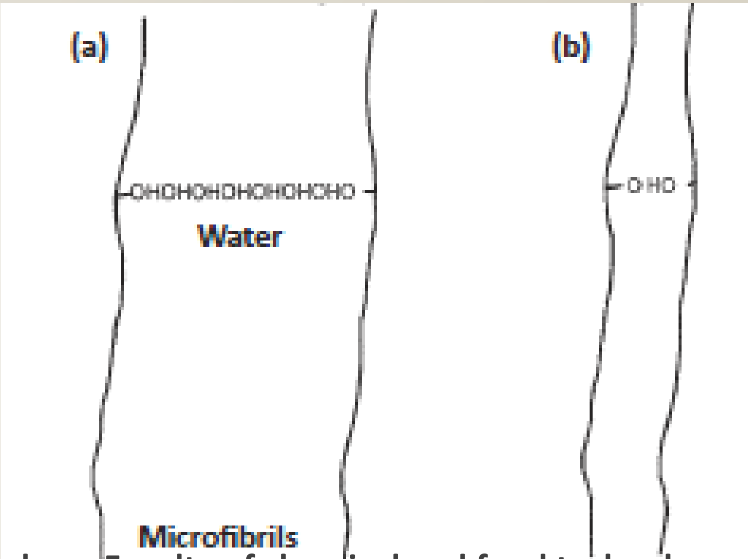


At this point, no water is present in the cell lumen, but the cell

wall is completely saturated. It can hold no more water between the microfibrils.

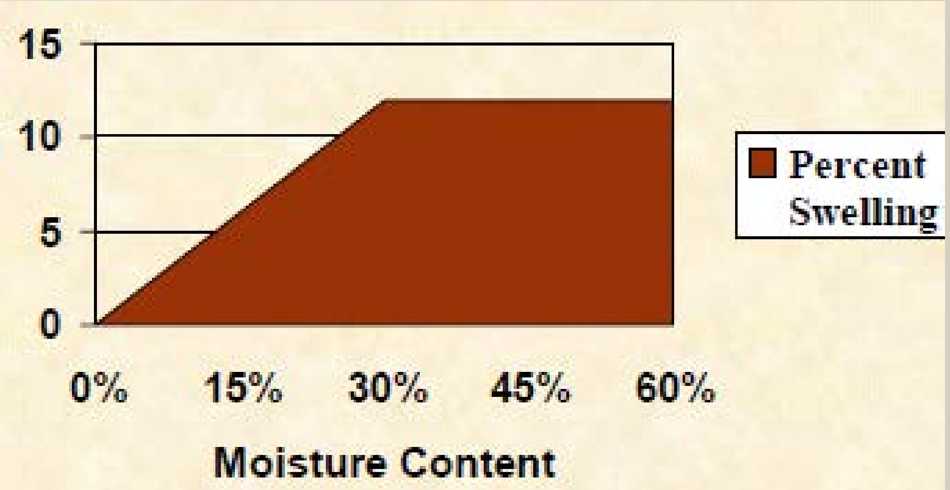
As wood **is dried further**, **bound water leaves the cell wall**, and cells start to **lose moisture** below the fsp.

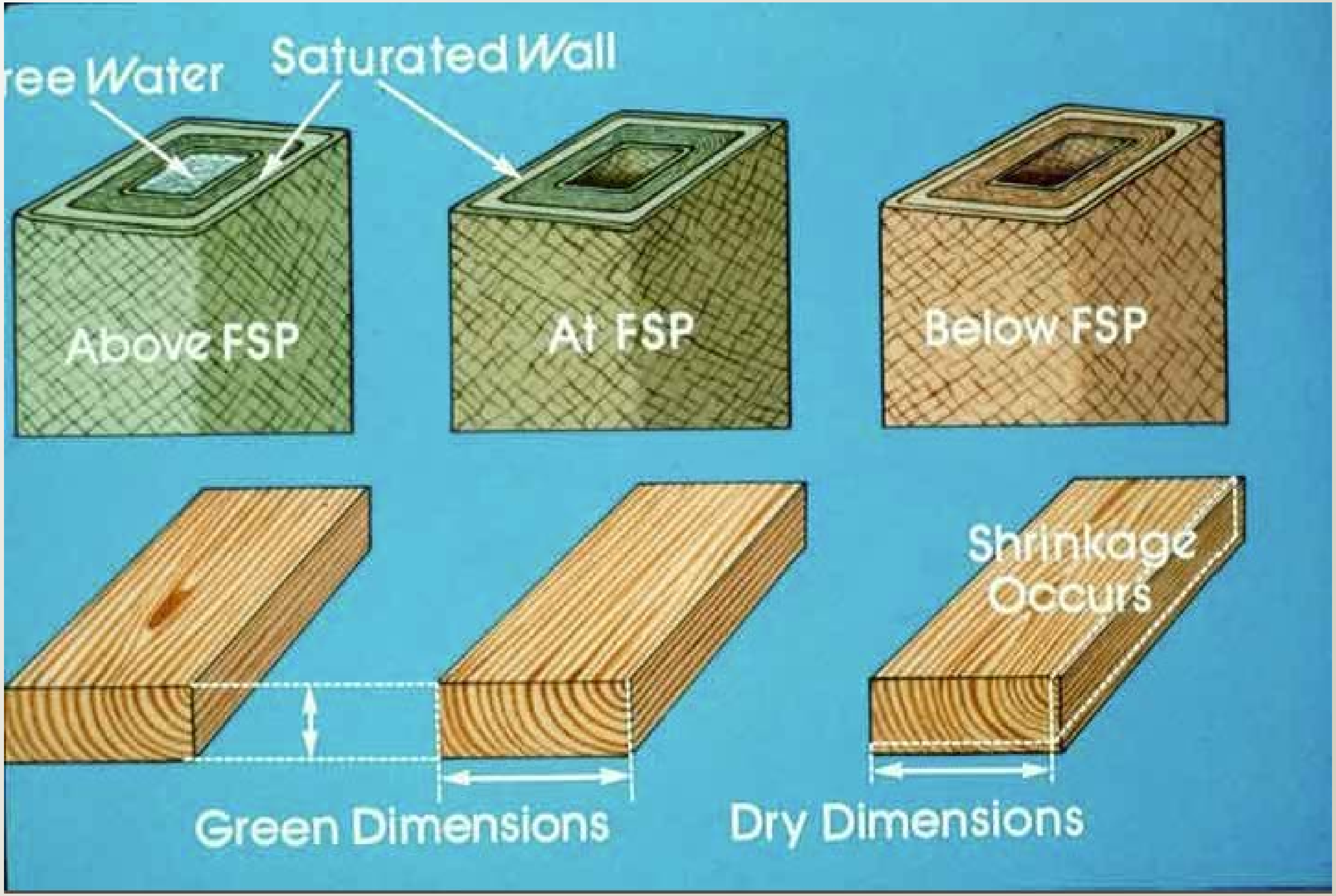
As water leaves and the microfibrils come closer together, **shrinking occurs.**



When **moisture is added to wood**, the process is **reversed**.
First, water enters the spaces between the microfibrils in the cell wall. The wood swells as the microfibrils are forced apart.

Once the fsp is reached, excess moisture **re-enters the wood lumens** and is held like water in a bucket. This water does not force the microfibrils apart since they are as far apart as possible at the fsp. Wood does **become heavier** as moisture is added above the fsp **but it does not swell** any further.




ree Water
Saturated Wall
Above FSP
At FSP
Below FSP
Shrinkage
Occurs
Green Dimensions
Dry Dimensions

Not completely reversible in swelling and shrinkage

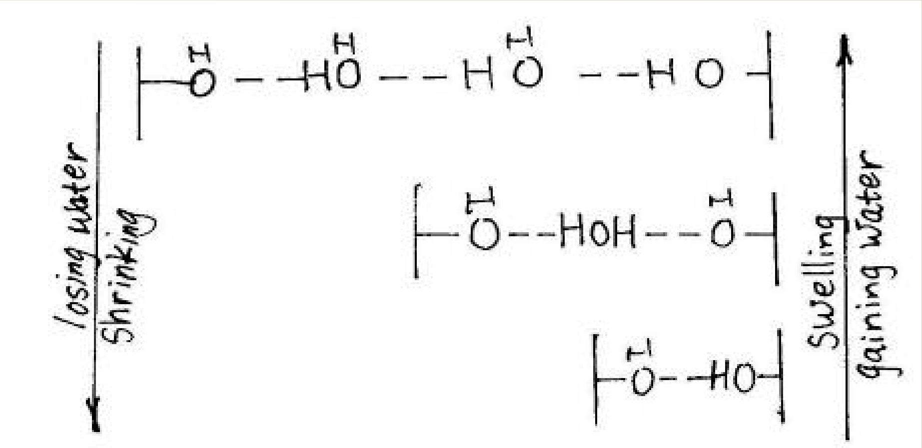
— due to the two different reference bases

— due to the hysteresis effect in the adsorption process

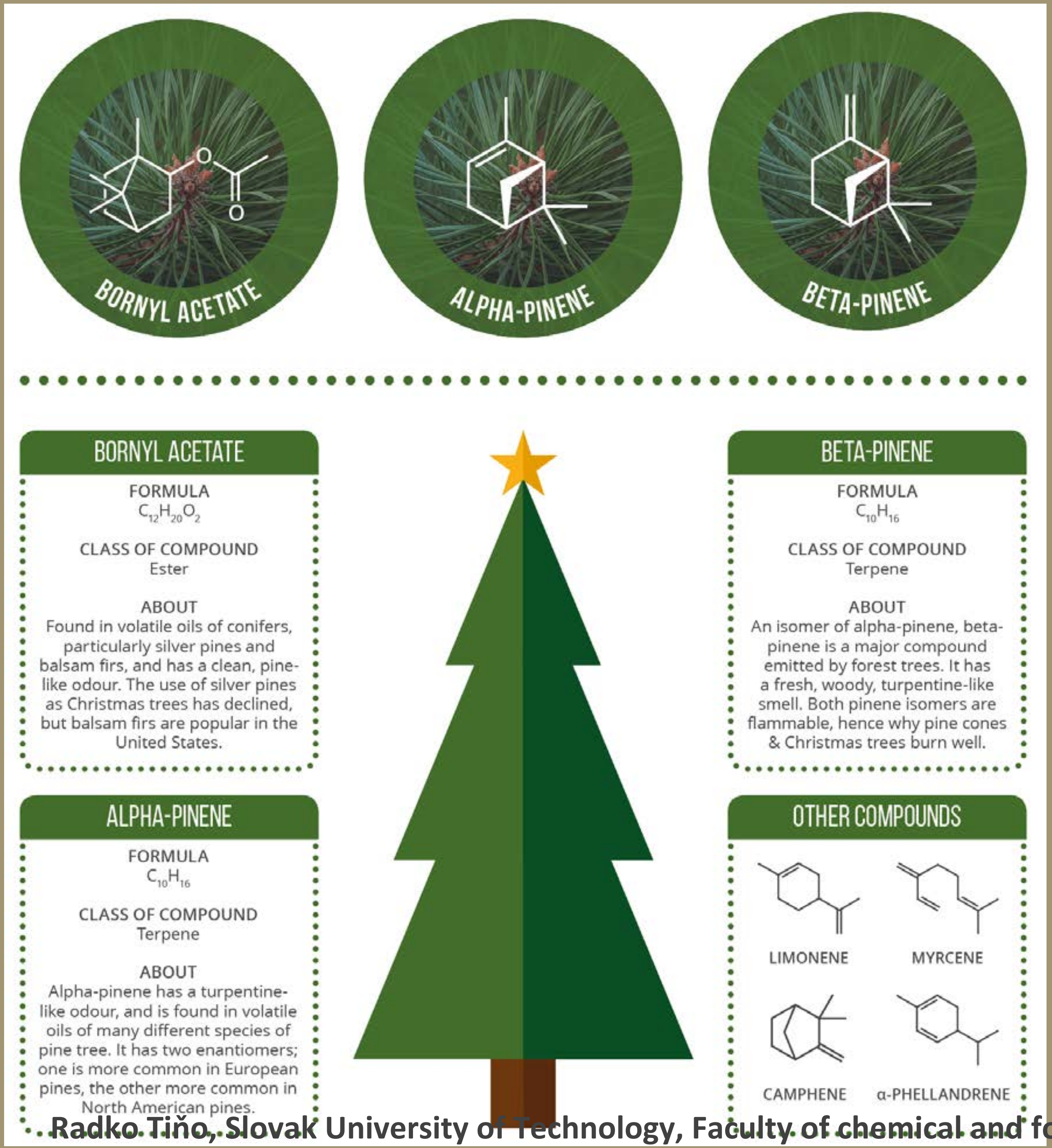
Mechanisms of shrinking and swelling of wood

— **Shrinking**: the collective effect of cellulose chains moving closer when losing water.

— **Swelling**: the collective effect of cellulose chains moving apart when gaining water.



Aroma of the Christmas tree



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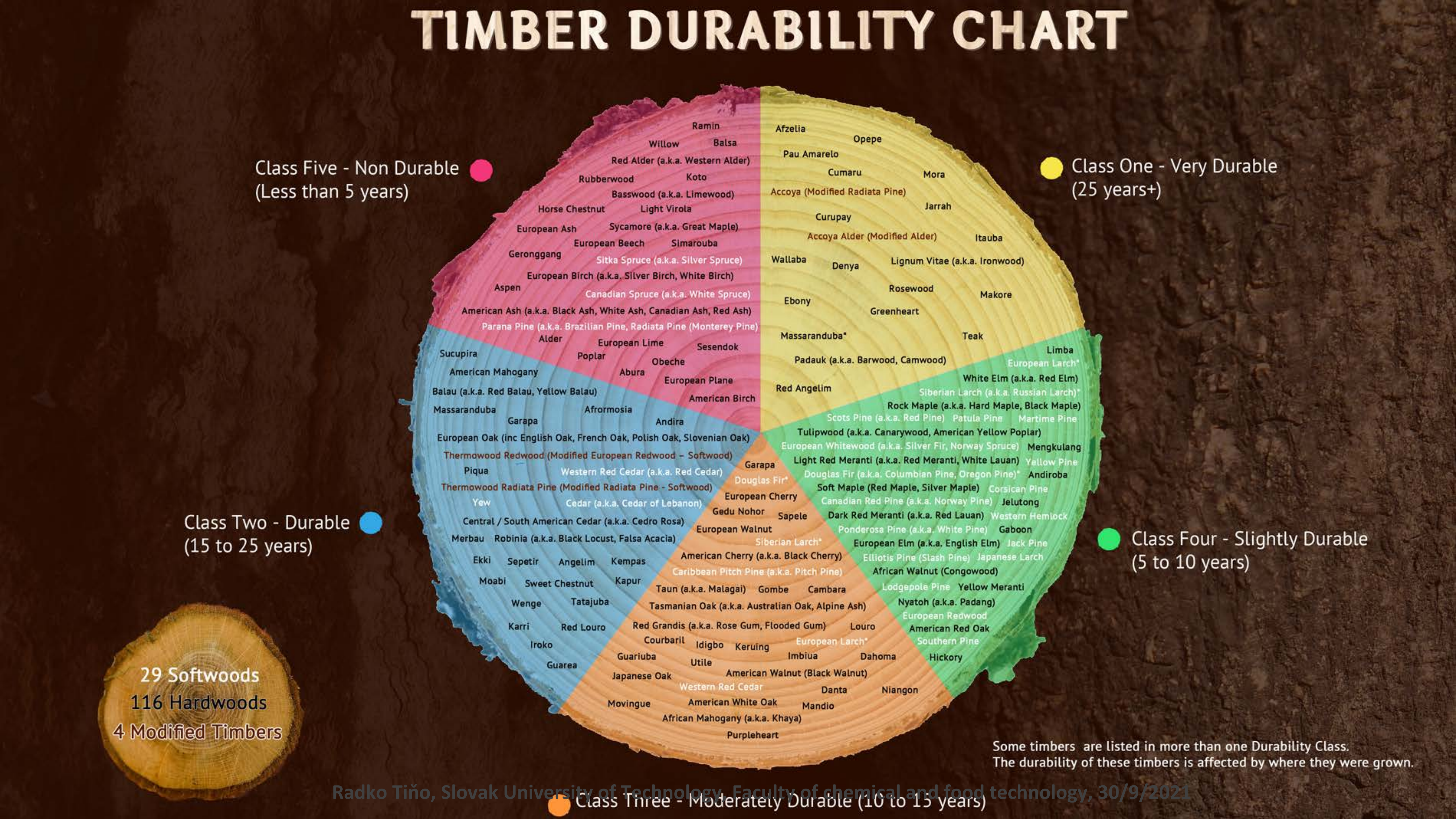
TIMBER DURABILITY CHART
Class Five - Non Durable (Less than 5 years)
Class One - Very Durable (25 years+)
Class Two - Durable (15 to 25 years)
Class Four - Slightly Durable (5 to 10 years)
Class Three - Moderately Durable (10 to 15 years)
Ramin
Willow
Balsa
Red Alder (a.k.a. Western Alder)
Rubberwood
Koto
Basswood (a.k.a. Limewood)
Horse Chestnut
Light Virola
European Ash
Sycamore (a.k.a. Great Maple)
European Beech
Simarouba
Geronggang
Sitka Spruce (a.k.a. Silver Spruce)
European Birch (a.k.a. Silver Birch, White Birch)
Aspen
Canadian Spruce (a.k.a. White Spruce)
American Ash (a.k.a. Black Ash, White Ash, Canadian Ash, Red Ash)
Parana Pine (a.k.a. Brazilian Pine, Radiata Pine (Monterey Pine)
Alder
European Lime
Sesendok
Poplar
Obeche
Abura
European Plane
American Birch
Afzelia
Opepe
Pau Amarelo
Cumaru
Mora
Accoya (Modified Radiata Pine)
Jarrah
Curupay
Accoya Alder (Modified Alder)
Itauba
Wallaba
Denya
Lignum Vitae (a.k.a. Ironwood)
Rosewood
Makore
Ebony
Greenheart
Massaranduba*
Teak
Padauk (a.k.a. Barwood, Camwood)
Red Angelim
Sucupira
American Mahogany
Balau (a.k.a. Red Balau, Yellow Balau)
Massaranduba
Afrormosia
Garapa
Andira
European Oak (inc English Oak, French Oak, Polish Oak, Slovenian Oak)
Thermowood Redwood (Modified European Redwood – Softwood)
Piqua
Western Red Cedar (a.k.a. Red Cedar)
Thermowood Radiata Pine (Modified Radiata Pine - Softwood)
Yew
Cedar (a.k.a. Cedar of Lebanon)
Central / South American Cedar (a.k.a. Cedro Rosa)
Merbau
Robinia (a.k.a. Black Locust, Falsa Acacia)
Ekki
Sepetir
Angelim
Kempas
Moabi
Sweet Chestnut
Kapur
Wenge
Tatajuba
Karri
Red Louro
Iroko
Guarea
Limba
European Larch*
White Elm (a.k.a. Red Elm)
Siberian Larch (a.k.a. Russian Larch)*
Rock Maple (a.k.a. Hard Maple, Black Maple)
Scots Pine (a.k.a. Red Pine)
Patula Pine
Martime Pine
Tulipwood (a.k.a. Canarywood, American Yellow Poplar)
European Whitewood (a.k.a. Silver Fir, Norway Spruce)
Mengkulang
Light Red Meranti (a.k.a. Red Meranti, White Lauan)
Yellow Pine
Douglas Fir (a.k.a. Columbian Pine, Oregon Pine)*
Andiroba
Soft Maple (Red Maple, Silver Maple)
Corsican Pine
Canadian Red Pine (a.k.a. Norway Pine)
Jelutong
Dark Red Meranti (a.k.a. Red Lauan)
Western Hemlock
Ponderosa Pine (a.k.a. White Pine)
Gaboon
European Elm (a.k.a. English Elm)
Jack Pine
Elliotis Pine (Slash Pine)
Japanese Larch
African Walnut (Congowood)
Lodgepole Pine
Yellow Meranti
Nyatoh (a.k.a. Padang)
European Redwood
American Red Oak
Southern Pine
Hickory
Garapa
Douglas Fir*
European Cherry
Gedu Nohor
Sapele
European Walnut
Siberian Larch*
American Cherry (a.k.a. Black Cherry)
Caribbean Pitch Pine (a.k.a. Pitch Pine)
Taun (a.k.a. Malagai)
Gombe
Cambara
Tasmanian Oak (a.k.a. Australian Oak, Alpine Ash)
Red Grandis (a.k.a. Rose Gum, Flooded Gum)
Louro
Courbaril
Idigbo
Keruing
European Larch*
Guariuba
Utile
Imbiua
Dahoma
Japanese Oak
American Walnut (Black Walnut)
Western Red Cedar
Danta
Niangon
Movingue
American White Oak
Mandio
African Mahogany (a.k.a. Khaya)
Purpleheart
29 Softwoods
116 Hardwoods
4 Modified Timbers
Some timbers are listed in more than one Durability Class.
The durability of these timbers is affected by where they were grown.

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