NATURAL POLYMERS 4
Lignin, Humic acids etc.

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Time schedule

LECTURE	SUBJECT
1	Introduction to the subject – Structure & Terminology of nature polymers, literature
2	Derivatives of acids – natural resins, drying oils, shellac
3	Waxes
4	Plant (vegetable) gums, Polyterpene – natural rubber (extracting, processing and modification), Taraxacum_kok-saghyz
5	Polyphenol – lignin, humic acids
6	Polysaccharides I – starch
7	Polysaccharides II – celullosis
8	Protein fibres I
9	Protein fibres II
10	Casein, whey, protein of eggs
11	Identification of natural polymers
	Laboratory methods of natural polymers' evaluation

Tree – Approximate Composition

PART	approx. % w/w
Tree stump + plant root system	20
Branches	15
Tree trunk – divided below	65
Treetop	5
Bark	5

The only approx. 55 % w/w of the Tree BIOMASS is so converted to the Sawtimber or the Wood pulp!

COMPOSITION of the WOOD (ELEMENTS)

Component	Content approx. (% w/w)
Carbon	50
Oxygen	42
Hydrogen	6
Nitrogen	1
Other elements	1

COMPOSITION of the WOOD (Polymers & Oligomers)

Component	Content approx. (% w/w)
Cellulose	40 – 50
Lignin	20 – 30
Hemicellulose	20 – 30
Water	Up to 14
Other (e.g. Terpenes, Waxes, Rosins, Fatty acids, Resin acids, Pectines etc.)	The Rest to 100

WOOD – Approximate Composition

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.[21] Wood also contains sulfur, chlorine, silicon, phosphorus, and other elements in small quantity.

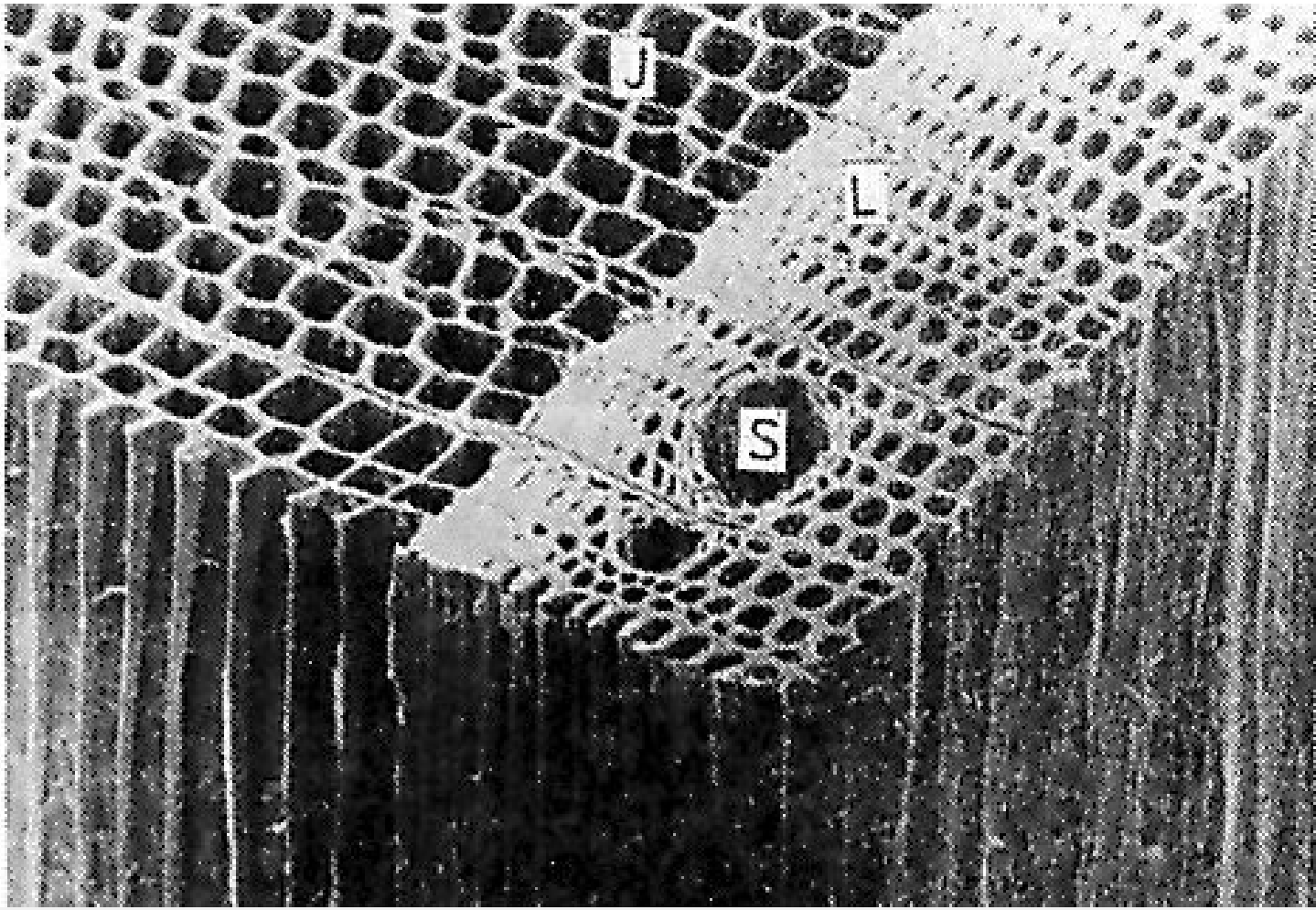
Aside from water, wood has three main components. Cellulose, a crystalline polymer derived from glucose, constitutes about 41–43%. Next in abundance is hemicellulose, which is around 20% in deciduous trees but near 30% in conifers. It is mainly five-carbon sugars that are linked in an irregular manner, 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. These three components are interwoven, and direct covalent linkages exist between the lignin and the hemicellulose. A major focus of the paper industry is the separation of the lignin from the cellulose, from which paper is made.

In chemical terms, the difference between hardwood and softwood is reflected in the composition of the constituent lignin. Hardwood lignin is primarily derived from sinapyl alcohol and coniferyl alcohol. Softwood lignin is mainly derived from coniferyl alcohol.[22]

Extractives

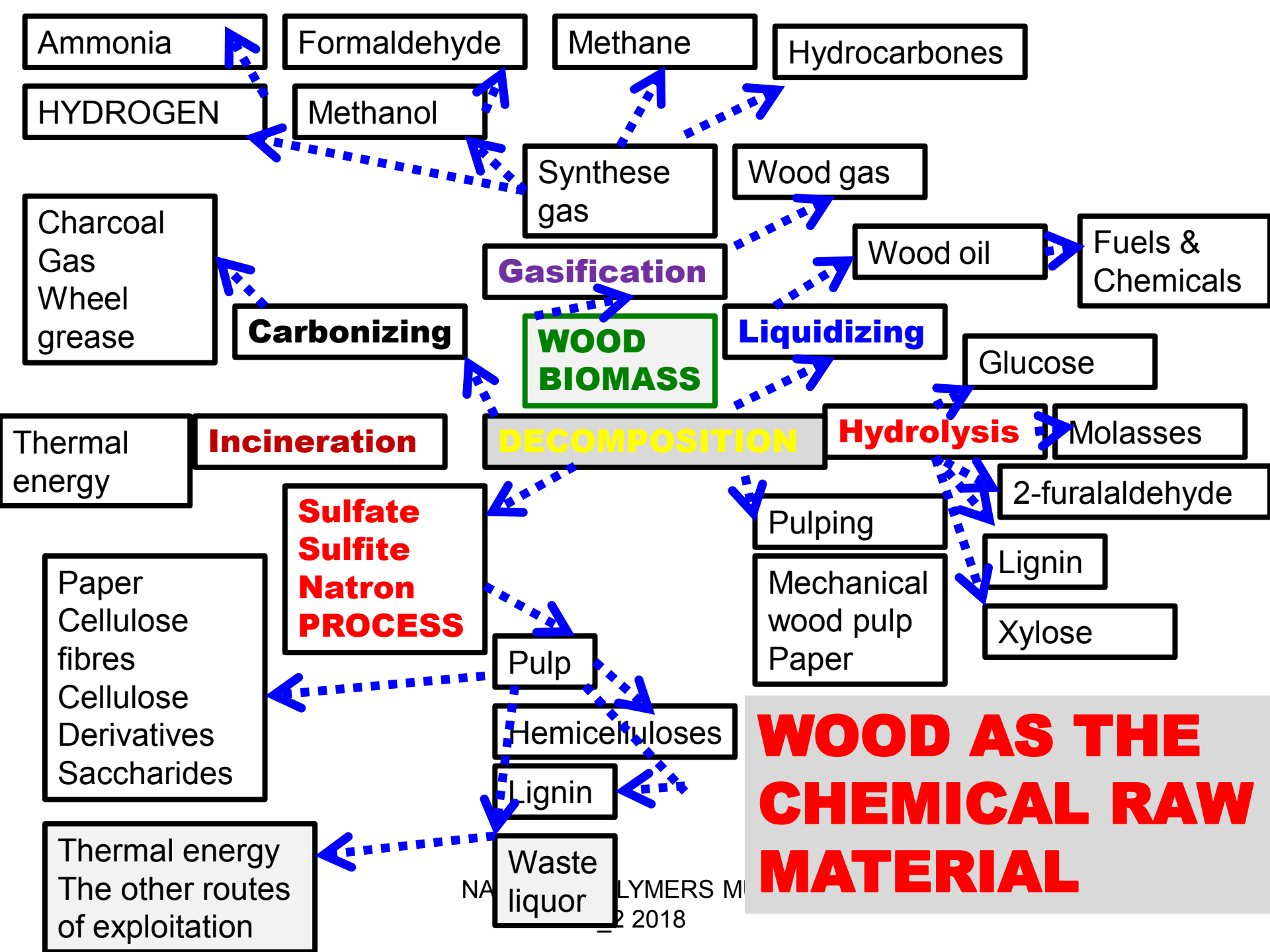
Aside from the lignocellulose, wood consists of a variety of low molecular weight organic compounds, called *extractives*. The wood extractives are fatty acids, resin acids, waxes and terpenes.[23] For example, rosin is exuded by conifers as protection from insects. The extraction of these organic materials from wood provides tall oil, turpentine, and rosin.

WOOD –EXAMPLE OF STRUCTURE
transversal sectional view



Anatomic Structure of the Coniferous species

J – Tracheides of the Spring Wood, L - Tracheides of the Summer Wood, S – Pitchy tubule


Ammonia
Formaldehyde
Methane
Hydrocarbones
HYDROGEN
Methanol
Synthese gas
Wood gas
Charcoal
Gas
Wheel grease
Gasification
Wood oil
Fuels & Chemicals
Carbonizing
WOOD BIOMASS
Liquidizing
Glucose
Thermal energy
Incineration
DECOMPOSITION
Hydrolysis
Molasses
2-furalaldehyde
Sulfate
Sulfite
Natron
PROCESS
Pulping
Lignin
Paper
Cellulose fibres
Cellulose Derivatives
Saccharides
Pulp
Mechanical wood pulp
Paper
Xylose
Hemicelluloses
Lignin
Thermal energy
The other routes of exploitation
Waste liquor
WOOD AS THE CHEMICAL RAW MATERIAL

WOOD GAS as CHEMICAL RAW MATERIAL & FUEL from RENEWABLE SOURCES

Component (% vol.)	Mean value
O_2 in the Sample*	1,815
CO_2	10,946
H_2	18,600
CO	22,050
CH_4	1,620
N_2	44,000
Ar**	0,569
ethane	0,018
ethylene	0,128
The other components	*0,254*
SUM (Total)	100,000

What is possible to be used for production of the Wood gas?

Which are the ADVANTAGES versus DISADVANTAGES of the Wood gas?

Wood gas in the HISTORY?

Manufacture of CELLULOSE

- **NATRON**
- **SULFITE**
- **SULFATE**

WE GO THROUGT IT IN DETAIL LATER

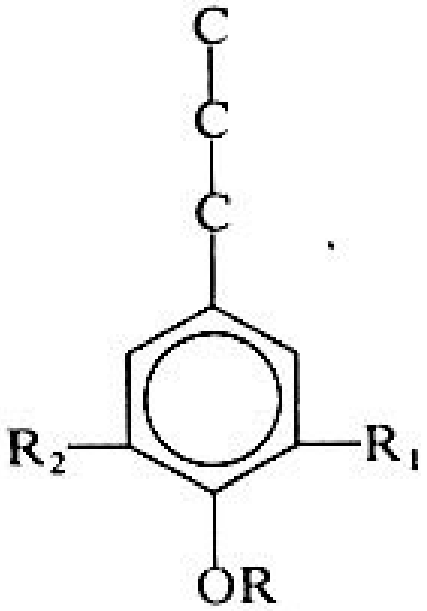
Polyphenolic compounds

- **Polyphenols are a Group of Chemical Compounds contained in Plants.** They are characterized by Presence more then one Phenolic unit or building block in a Molecule.
- **Polyphenols are divided in general**:
  - **Hydrolysable tannins (esters of gallic acid and glucose or the other sachcarides)**
  - **Phenylpropanoides, e.g. lignins,**
  - **Flavonoids**
  - **Condensed tannins**

LIGNIN 1

- **The main NONcelullosis part of Wood (20 – 30 % w/w), coniferous tree has more Lignin then broad-leaved tree**
- **It forms the adhesive component between celullose Fibres > WOOD is so the COMPOSITE MATERIAL!**
- **Amorphous macromolecular substance , a Mixture of up to now not entirely revealed composition > there are many Formulas of Lignin (see the next slides)**
- **Lignin is probably chemically bonded to POLYSACCHARIDES in the Wood**
- **PHENYLPROPANE derivatives are considered as the Basic building unit of the Lignin**

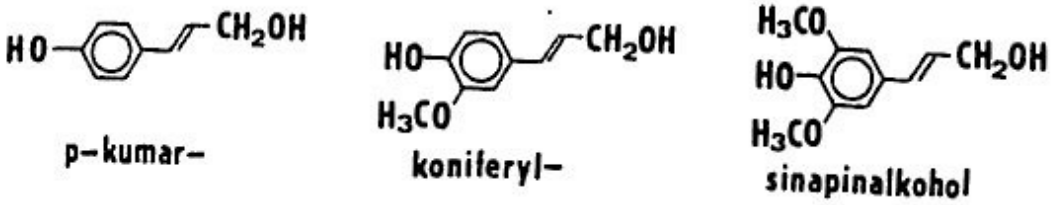
LIGNIN 2



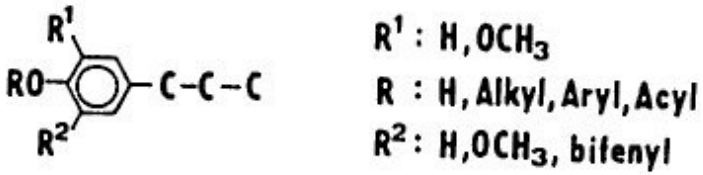
kde R = H nebo alkyl, aryl, acyl aj.
R_1 = $-OCH_3$ nebo H
R_2 = $-OCH_3$ nebo H, —C (bifenyl, fenylkumaron) aj.

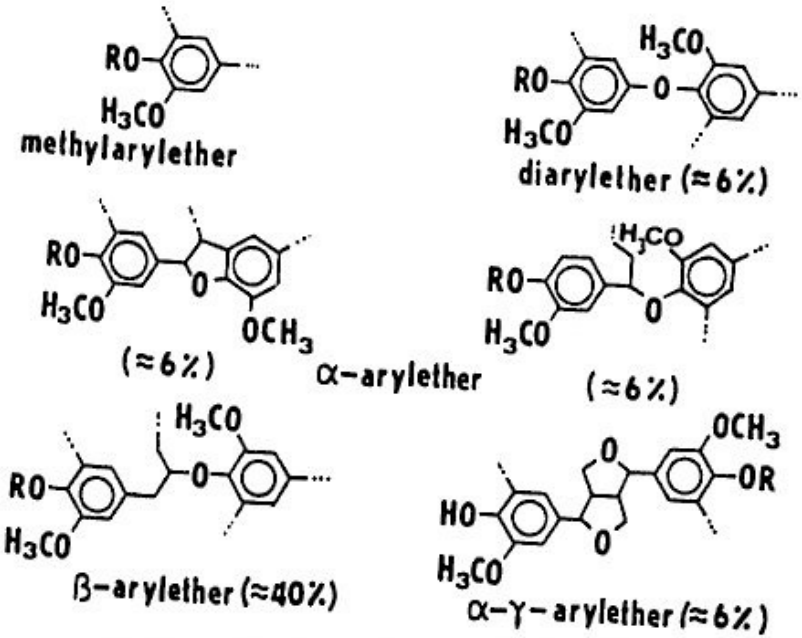
Derivatives of PHENYLPROPANE

LIGNIN 3



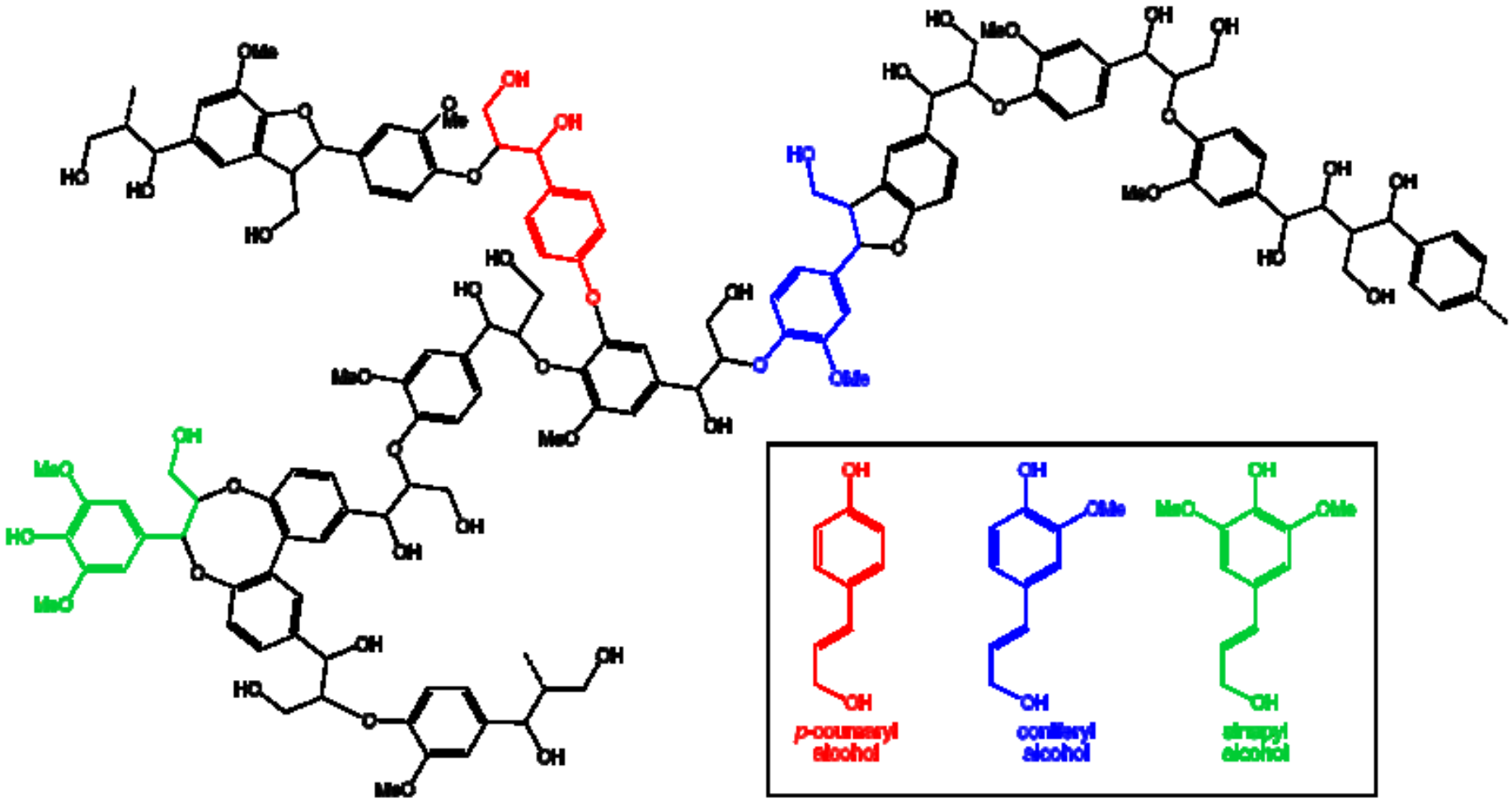
Derivatives PHENYLPROPANE creating LIGNIN



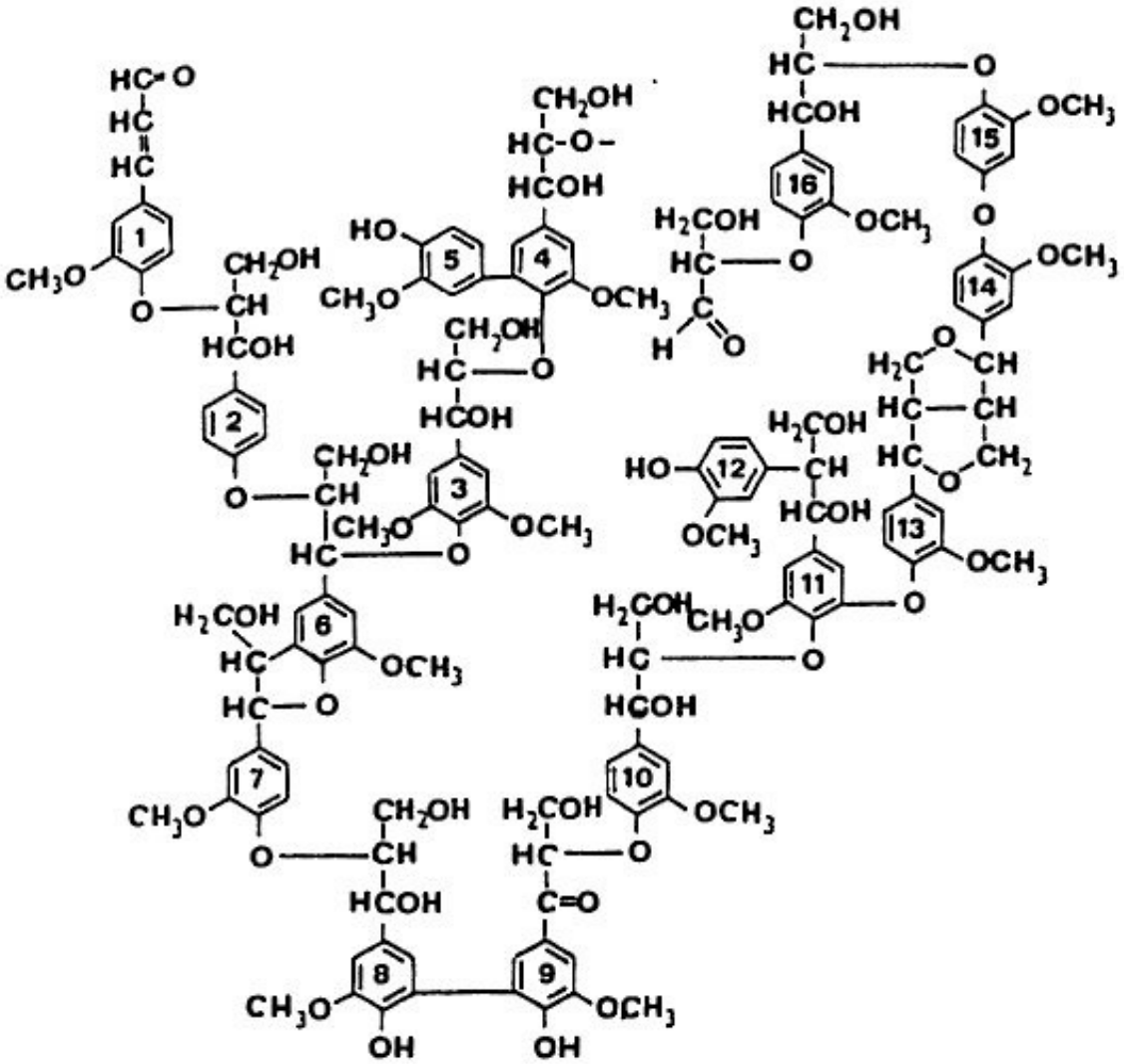


Crosslinking of lignin via ETHEREAL BRIDGE

LIGNIN 4 – POSSIBLE FORMULAS I

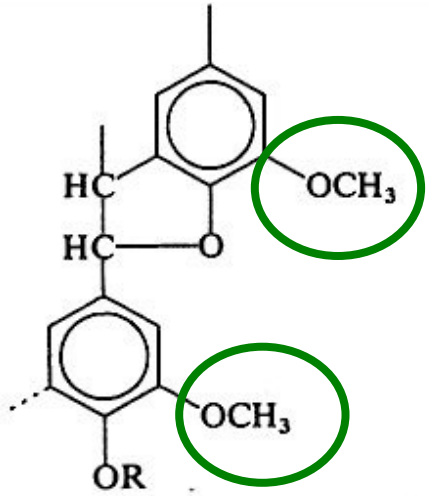


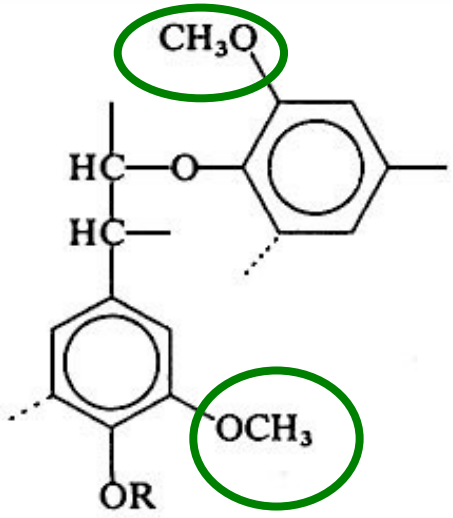
LIGNIN 5 –POSSIBLE FORMULAS II



LIGNIN 6 – How is it gained?

- **LIGNIN is the WASTE MATERIAL at Production of the Chemical Production of the Pulp**
- **Problem of its Utilisation is, that LIGNIN is not well defined Substance, but LIGNIN from various Sources is different as to the Composition**
- **Reactive point is the Ethereal Bridge > the Possibility to produce Methanol via Cleavage –OCH_3 Group**

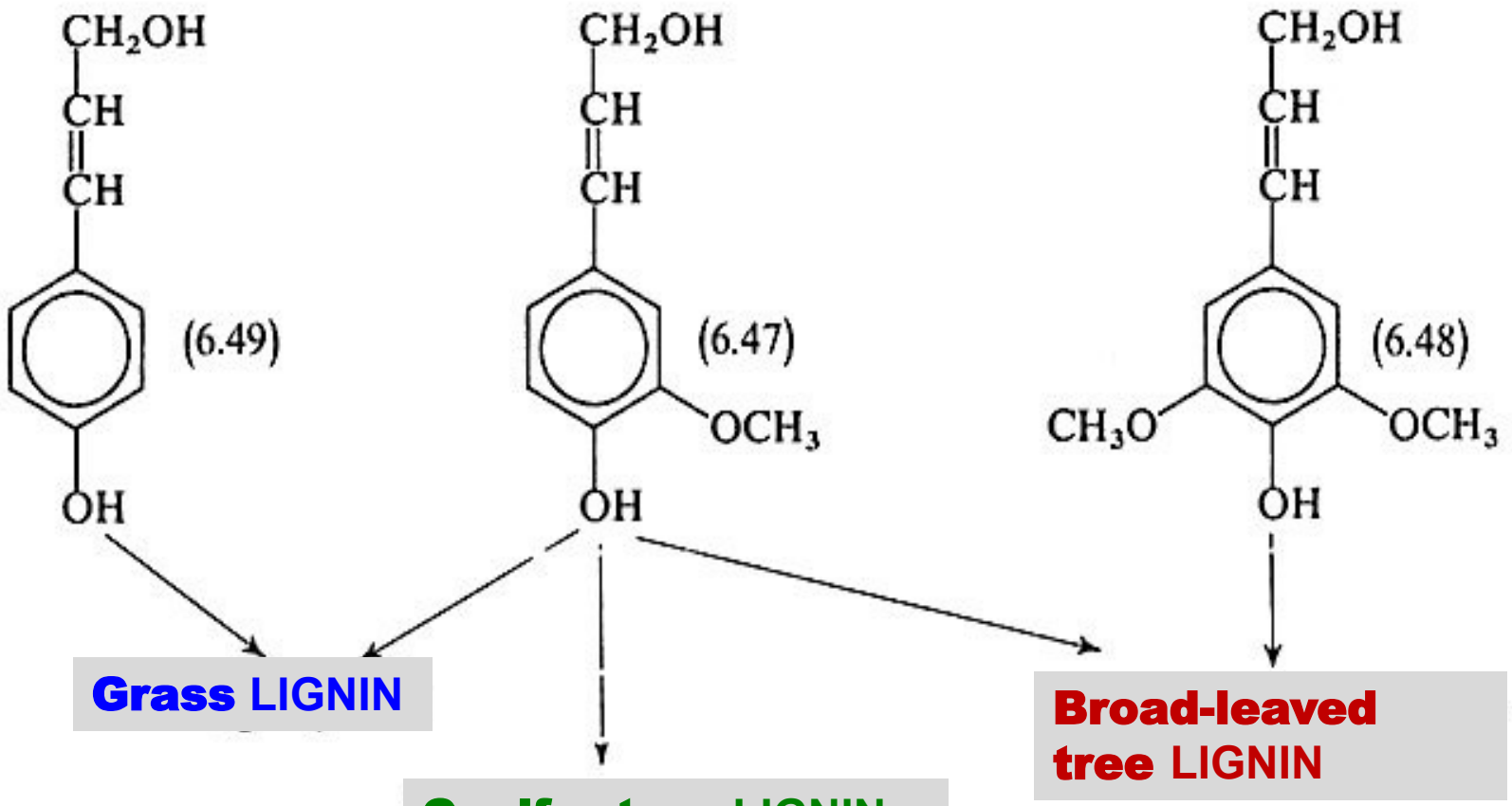




β-arylether
~ 40 %

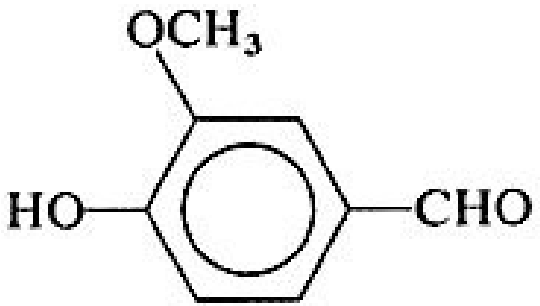
LIGNIN 7 – Problem of its Utilisation is, that LIGNIN is not well defined Substance, but LIGNIN from various Sources is different as to the Composition

The BASIC SUBSTANCES for various LIGNINS

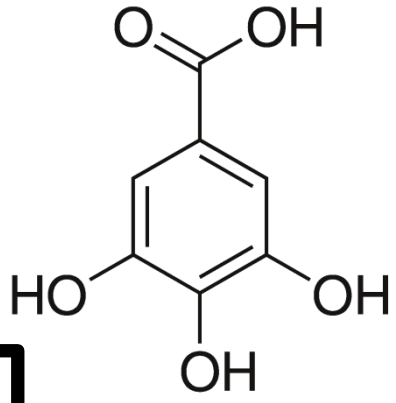


LIGNIN 8 – Chemical and other Utilisation

Chemical – it is up to now only the Minimal one



Vanillin



Gallic acid

vá

Other Utilisation:

The main part,so called „**Waste liquor**“, is combusted up to now

VALORIZATION OF LIGNIN – CHEAP WASTE POLYMER IS WAITING FOR YOU!

LIGNIN 9 – Chemical and other Utilisation

Chemical – it is up to now only the Minimal one

The very interesting Process of the Chemical Utilisation of LIGNIN has appeared last year on Internet. It should result up to terephthalic acid

LIGNIN 10 – the LATEST LITERATURE

It will be issued in 2018 or 2019

Lignin Valorization:

Emerging Approaches

(RSC Publishing, Royal Society Chemistry)

Editor: Gregg T Beckham

About this book

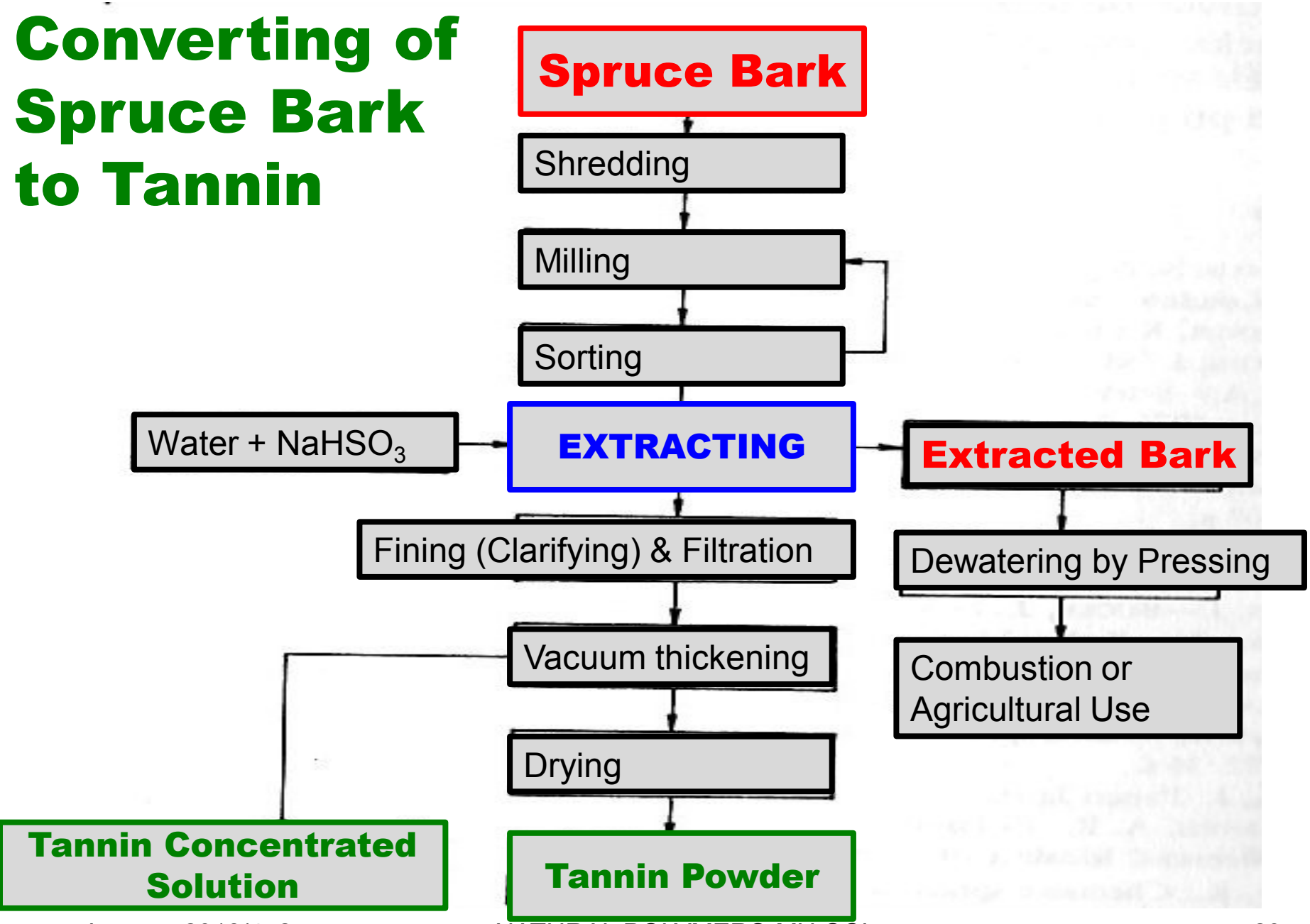
Lignin, an aromatic biopolymer found in plant cell walls, is a key component of lignocellulosic biomass and generally utilized for heat and power. However, lignin's chemical composition makes it an attractive source for biological and catalytic conversion to fuels and chemicals. Bringing together experts from biology, catalysis, engineering, analytical chemistry, and techno-economic/life-cycle analysis, **Lignin Valorization** presents a comprehensive, interdisciplinary picture of how lignocellulosic biorefineries could potentially employ lignin valorization technologies.

Chapters will specifically focus on the production of fuels and chemicals from lignin and topics covered include (i) methods for isolating lignin in the context of the lignocellulosic biorefinery, (ii) thermal, chemo-catalytic, and biological methods for lignin depolymerization, (iii) chemo-catalytic and biological methods for upgrading lignin, (iv) characterization of lignin, and (v) techno-economic and life-cycle analysis of integrated processes to utilize lignin in an integrated biorefinery.

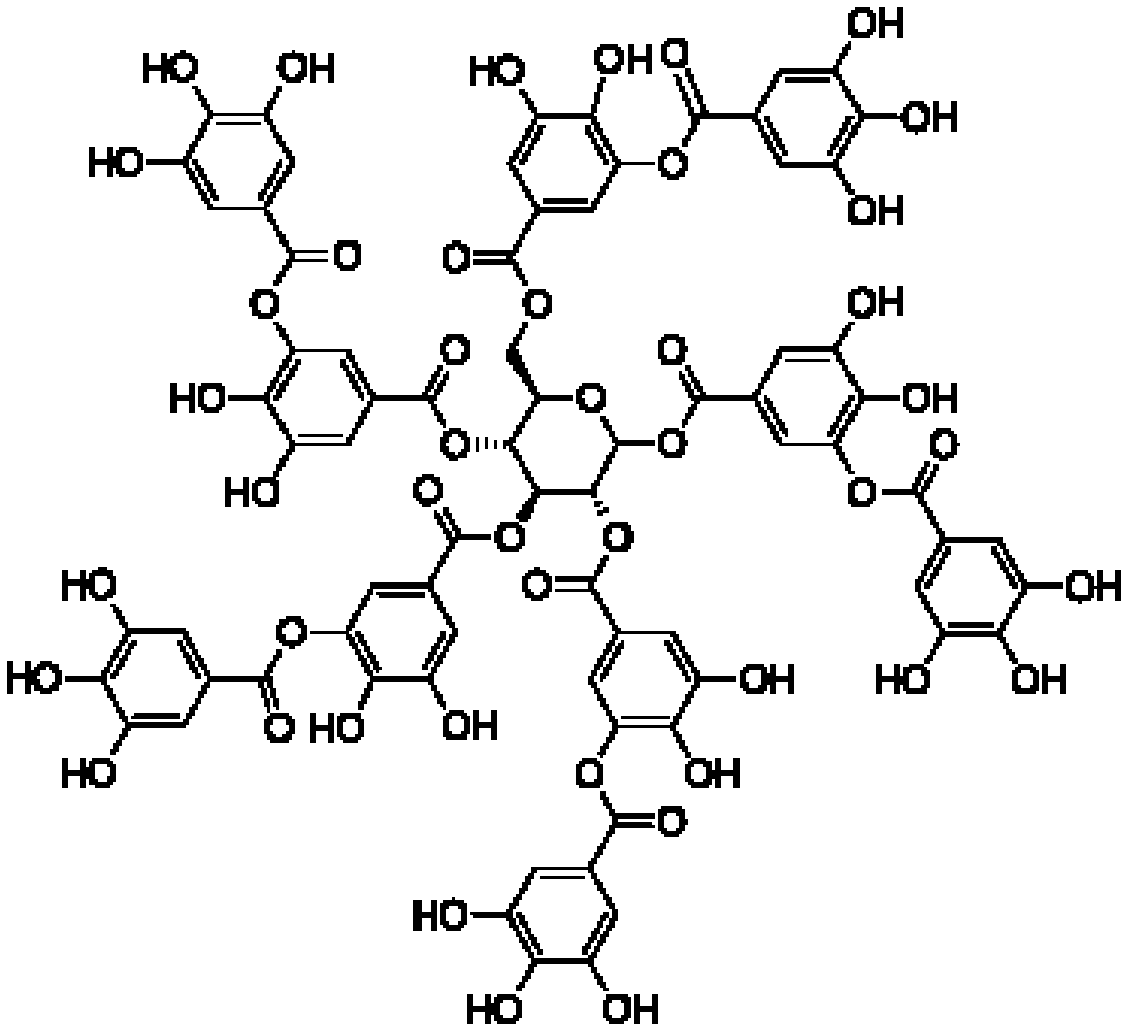
Tannins

- **Tannins** are the Plant **Polyphenols** of the bitter or/and astringent taste, coagulating proteins and alkaloids
- **Tannins** **are used for** **Vegetable tanning of Rawhide to Leather**
- **Tannins** are from the Chemical point of view big **Polyphenolic Compounds**, which contains hydroxyl and carboxyl Groups possessing ability to bound themselves to Proteins and other Macromolecules
- **Tannins** have usually MW of approx. from 500 to 3 000 g/mol.

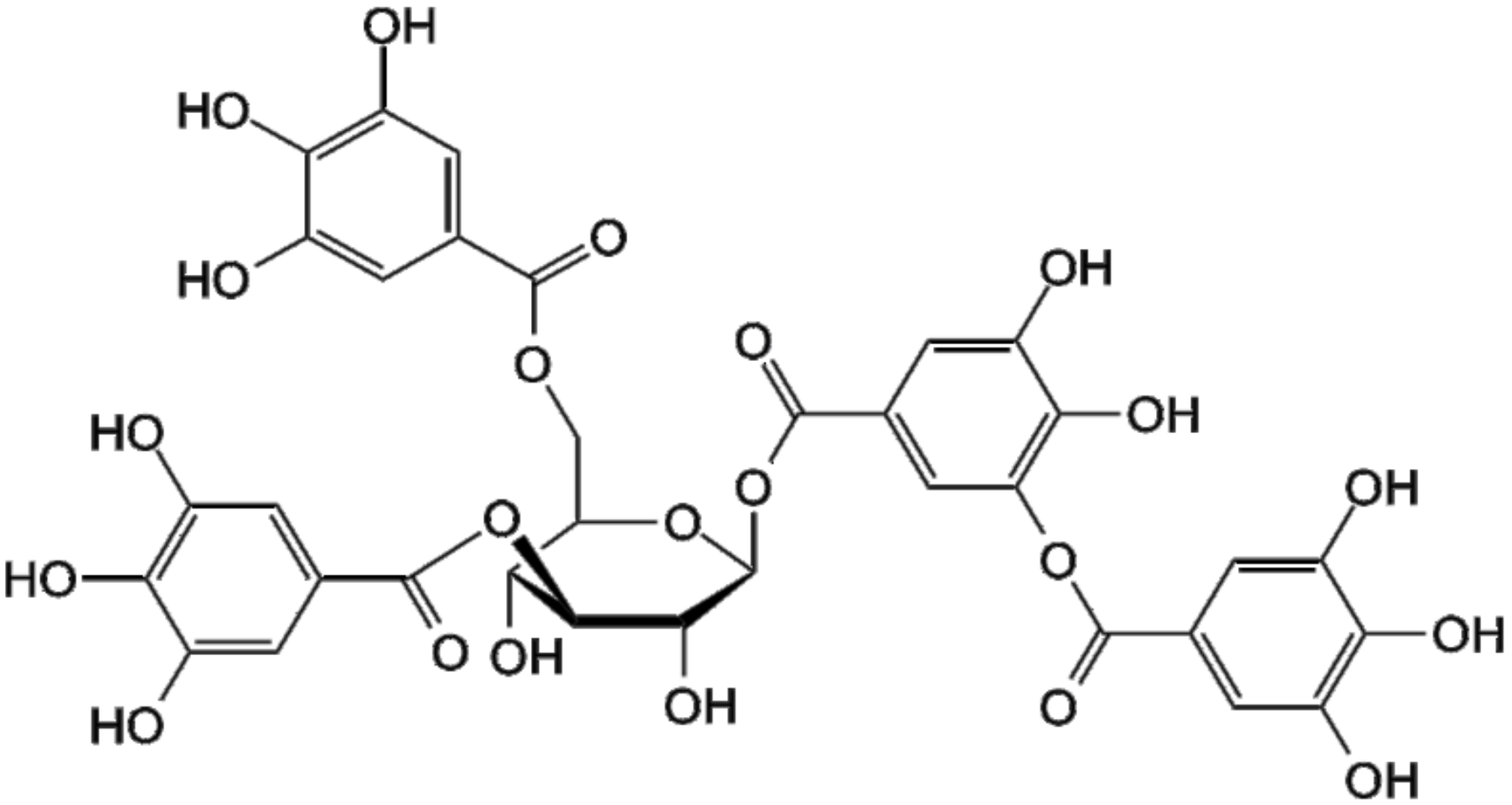
Converting of Spruce Bark to Tannin



Tannin – one of the POSSIBLE STRUCTURES



Tannin – other of the POSSIBLE STRUCTURES



Tannin = tannic acid or digallic acid or gallotannic acid or gallotannin

Product SIGMA ALDRICH

Tannic acid

5 Products

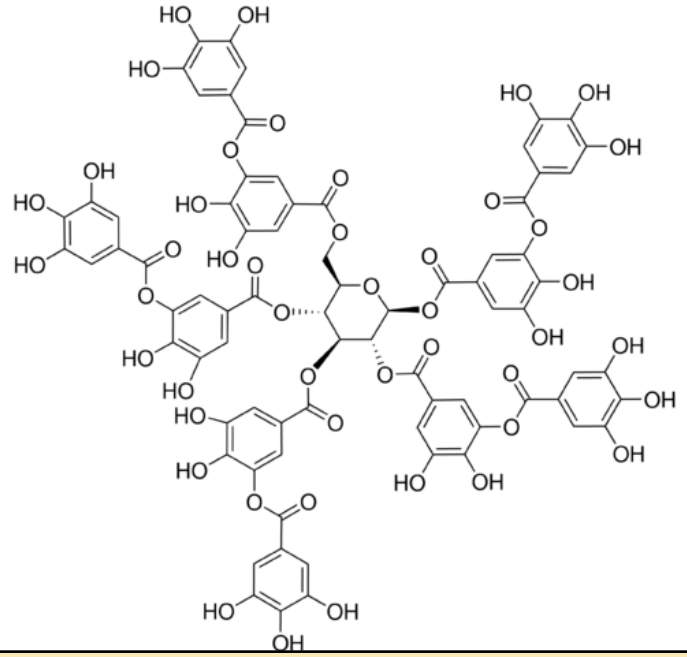
Synonym: Gallotannin, Tannin

CAS Number: 1401-55-4

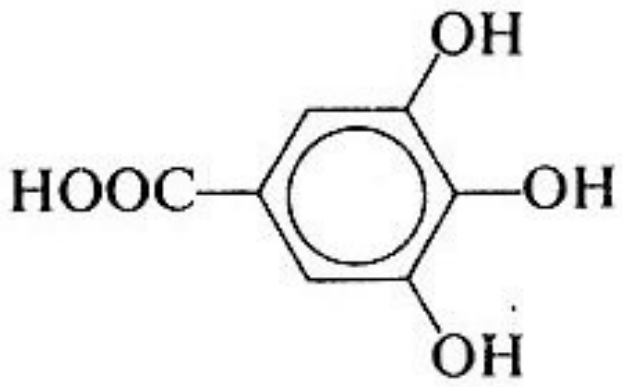
Empirical Formula (Hill Notation):
$C_{76}H_{52}O_{46}$

Molecular Weight:
1701.20

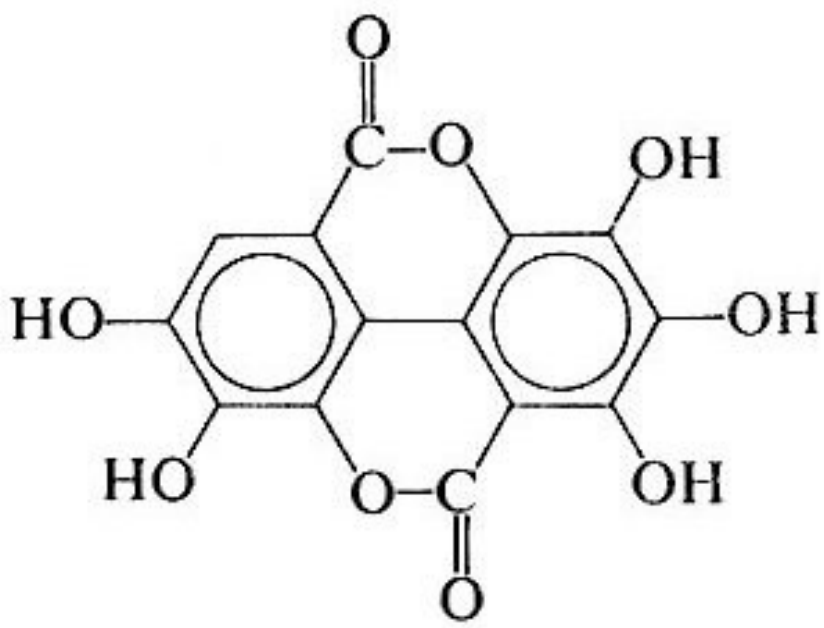
Beilstein Registry Number:
8186396



Properties	
Chemical formula	$C_{76}H_{52}O_{46}$
Molar mass	1701.19 g/mol
Density	2.12g/cm^3
Melting point	decomposes above 200 °C
Solubility in water	2850 g/L
Solubility	100 g/L in ethanol 1 g/L in glycerol and acetone insoluble in benzene, chloroform, diethyl ether, petroleum, carbon disulfide, carbon tetrachloride.
Acidity (pK_a)	ca. 10



Gallic acid



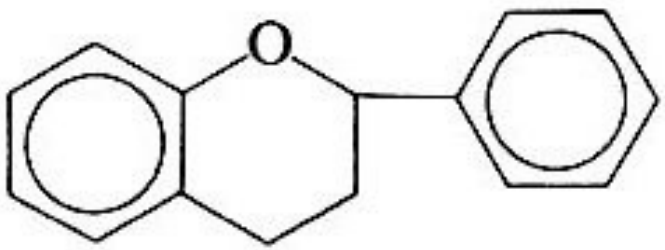
Ellagic acid

Hydrolysable tannins = Gallotannic acid

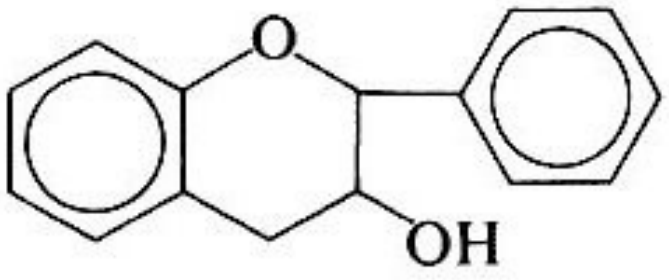
+

Bound saccharides

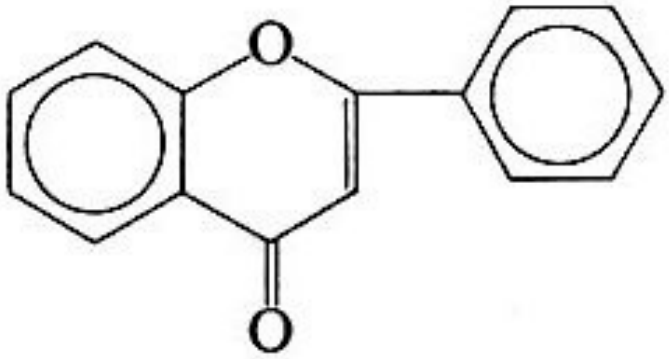
Flavonoids > condensed tannins



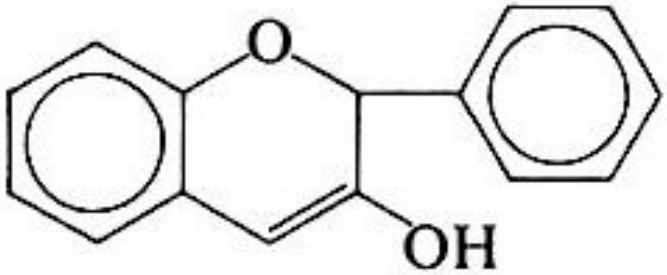
flavan



flavan-3-ol (katechin)

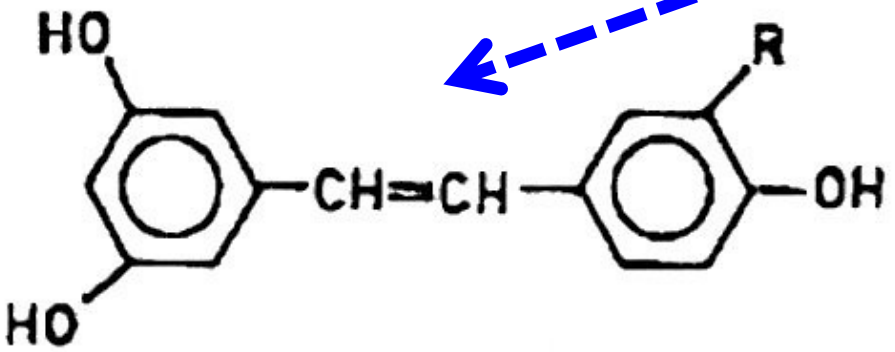


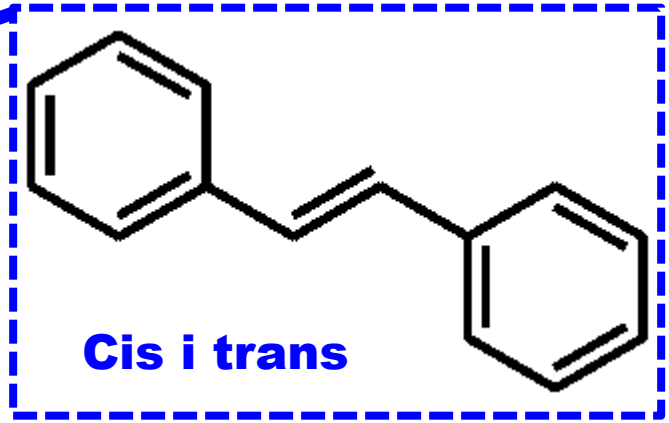
flavón

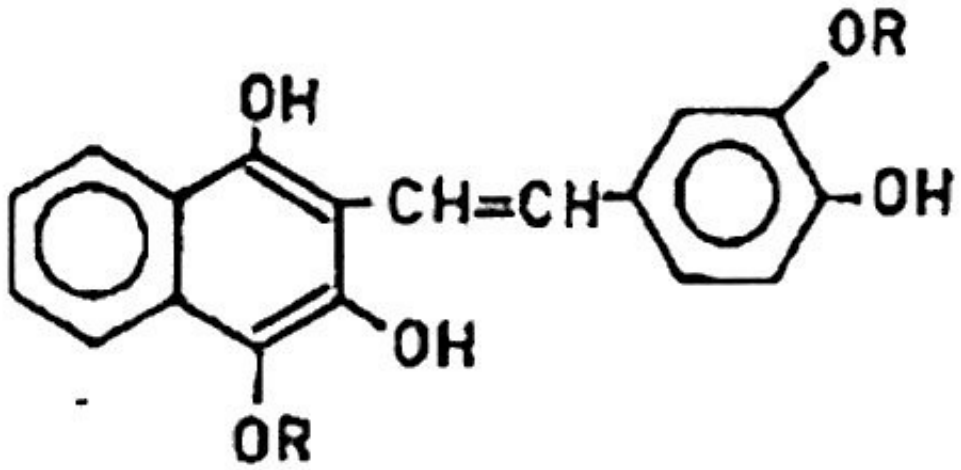


antokyanidín

Tannins derived from STILBENE







piceatanol

Flavonoids > condensed tannins

&

Hydrolysable tannins = Gallotannic acid

& Ellagic acid

+Bound saccharides

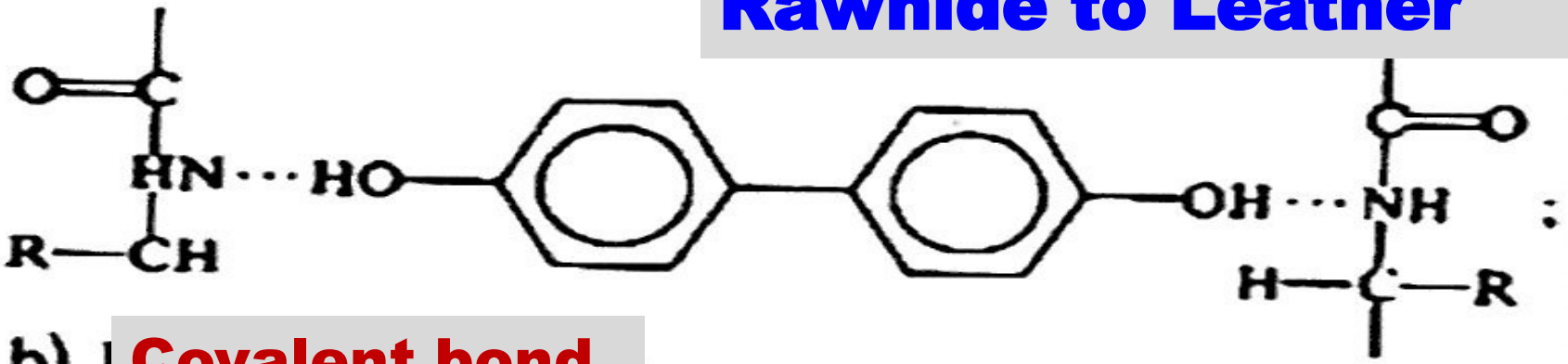
&

Tannins derived from STILBENE

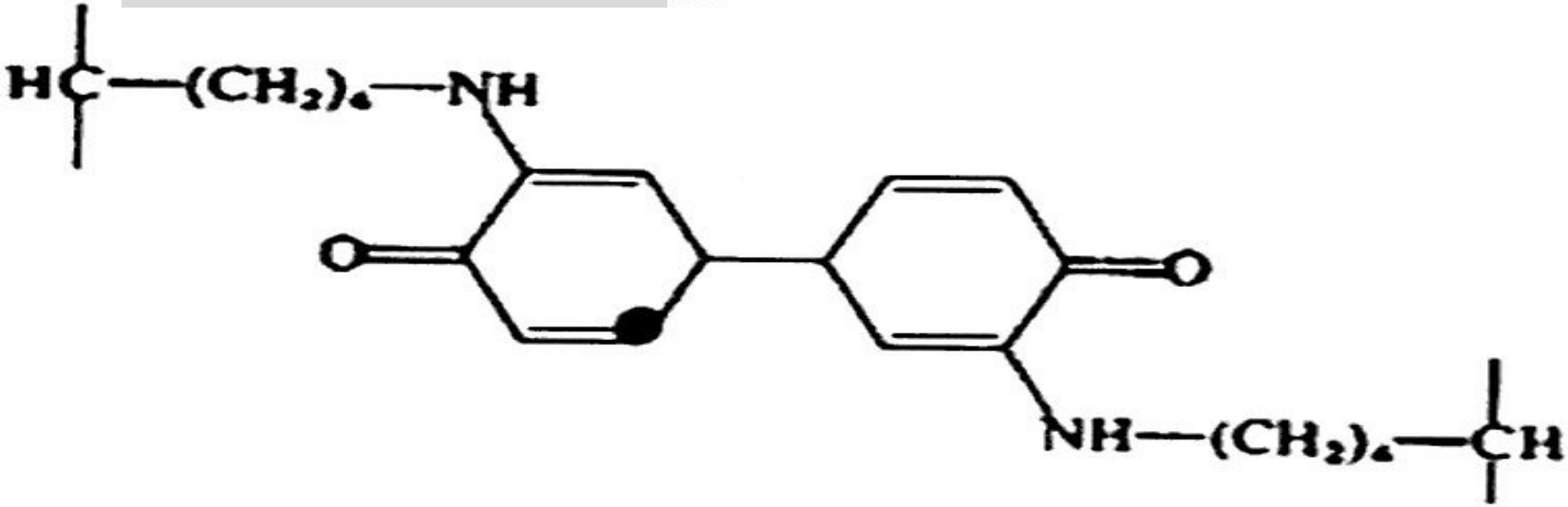
They are frequently occurring together in one Plant extract

Vegetable tanning of Rawhide to Leather

a) **Hydrogen bond**



b) **Covalent bond**



Interaction of Tannins with Collagene

Iron gall ink ink 1

Iron gall ink (also known as **iron gall nut ink**, **oak gall ink**, and **common ink**) is the Ink purple-black colour, made from salts of Iron and taninn from plant sources. It is concerned organometallic compound dispersed in Water, in which is stabilized by the binding agent and this additive ensures remaining of the pigment Dispersion in the Solution. It currently used in Europe 12.Century since.

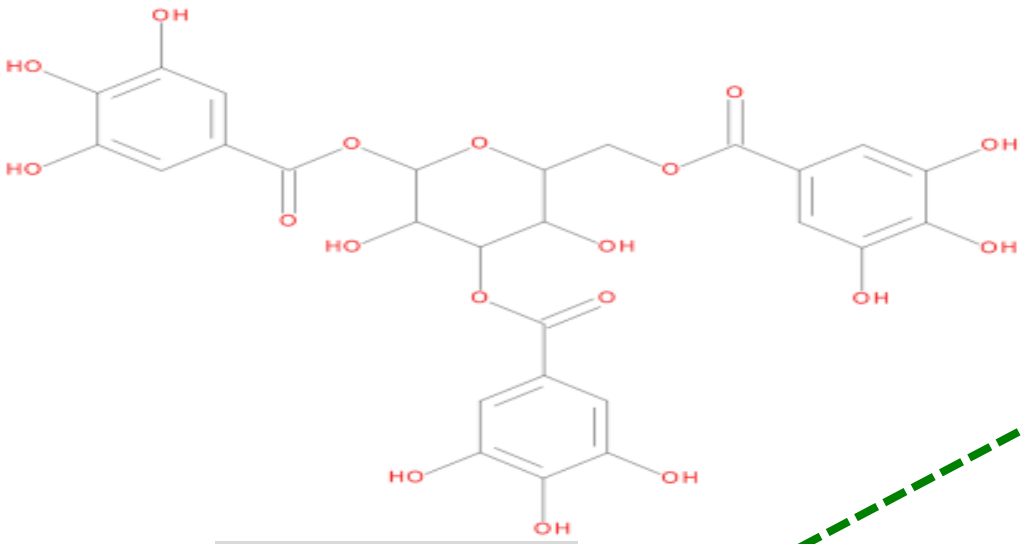
gallnut, gall-apple >

Iron gall ink ink 2

Simple Recipe

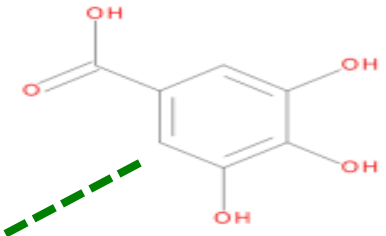
- **Tannin = tannic acid**
- Green vitriol ($FeSO_4$)
- ARABIC GUM > **Plant gum**
- Water

Iron gall ink ink 3

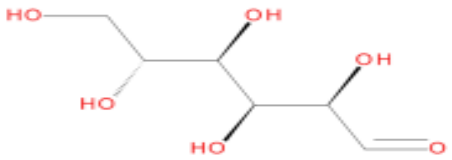


Tannic acid

+ H_2O

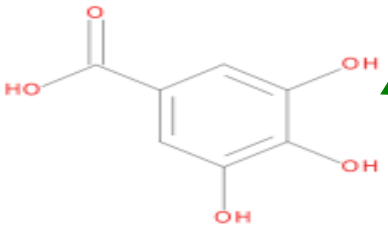


Gallic acid

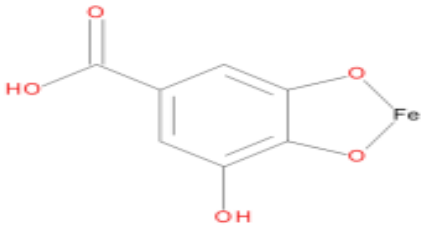


Glucose

Fe^{+2}



+ $FeSO_4$ →

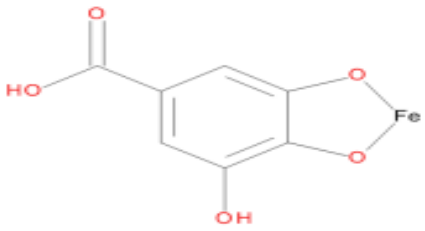


+ H_2SO_4

Ferrous Gallic salt

Fe^{+3}

2



+ 1/2 O_2 →

+ H_2O

Ferric Gallic salt

Fe^{+2} Iron gall ink 4 Fe^{+3}

Chemical Basis of the Iron gall ink is as follows:

- Reaction of the Iron Oxidation number/state Change ions' from FERROUS (Fe^{2+}) to FERRIC (Fe^{3+}) state by atmospheric OXYGEN and via this way Change of the Colour from the Pale-grey solution to Purple-black

Chemical Basis of the Iron gall ink BLEACHING is as follows:

- Reaction of the Iron Reduction from FERRIC (Fe^{3+}) to FERROUS (Fe^{2+})

HOW TO REFRESH THE REDUCED FERROUS (Fe^{2+}) ?

- OXIDATION from FERROUS (Fe^{2+}) to FERRIC (Fe^{3+}) state

DURABILITY OF THE Iron gall ink is increased by the Reaction with Cellulose or Collagen

U.S. government "standard ink" formula (1935)

- 11.7 g tannic acid
- 3.8 g gallic acid $C_6H_2(OH)_3COOH$
- 15 g iron(II) sulfate
- 3 cm^3 hydrochloric acid (used to prevent sediment forming)
- 1 g carbolic acid (phenol) C_6H_5OH (biocide)
- 3.5 g china-blue aniline dye (water-soluble)
- 1000 cm^3 distilled water[11]

German regulation for *Urkundentinte* inks (1933)

- In a litre of ink there has to be at least 27 g of tannic acid and gallic acid, and at least 4 g of iron content. The maximum iron content is not allowed to surpass 6 g / l.
- After 14 days' storage in a glass container the ink is not allowed to have stained the glass or show sedimentation.
- Eight-day-old writings after washing with water and alcohol must remain very dark.
- The ink has to flow easily from the pen, and may not be sticky even immediately after drying![10]

Indian Standard 220 (1988)

In India, the IS 220 (1988): Fountain Pen Ink – Ferro-gallo Tannate (0.1 percent iron content) Third Revision standard, which was reaffirmed in 2010, is in use. This Indian Standard was adopted by the Bureau of Indian Standards on 21 November 1988, after the draft finalized by the Inks and Allied Products Sectional Committee had been approved by the Chemical Division Council. IS 220 prescribes the requirements and the methods of sampling and tests for ferrogallo tannate fountain pen inks containing not less than 0.1 percent of iron.[12]

- 4.0 g tannic acid
- 1.5 g gallic acid
- 5.5 g ferrous sulphate crystals $FeSO_4 \cdot 7H_2O$
- 5.0 g concentrated hydrochloric acid
- 5.0 g dye, ink blue (see IS 8642 : 1977)
- provisional dye (for inks other than blue black) As advised by supplier
- phenol (see IS 538 : 1968)
- distilled water (to make the total volume one litre).

INK versus China ink

- **INK is composed from: ……**
- **China ink is composed from : ……**

Tanins & Food Industry

- **Clarifying of the Fruit juice in combination with Gellatin**
- **It coagulate the Proteins**

Tanin – quite new Use

A new method for preparing tannin-based foams

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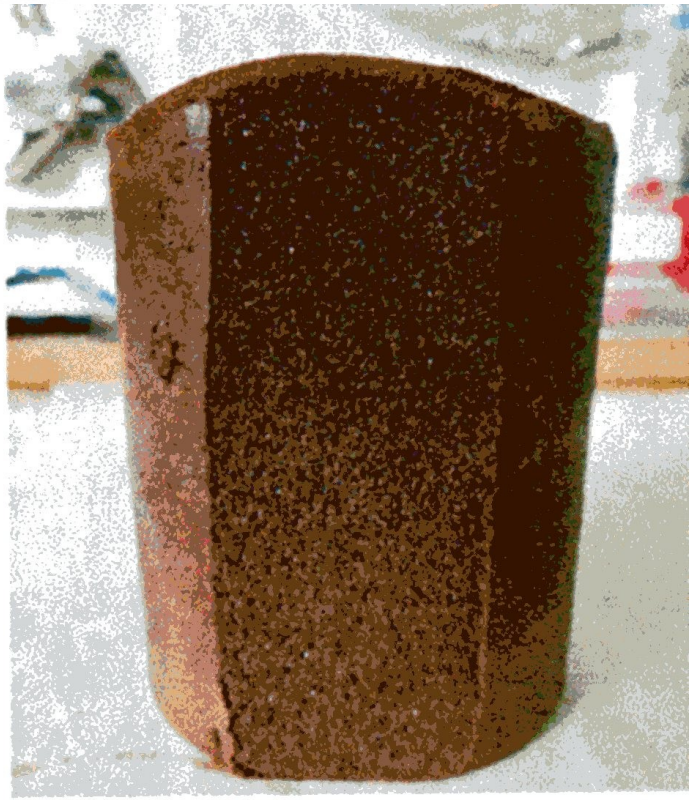
It must be CROSSLINKED by something!



Humin substances

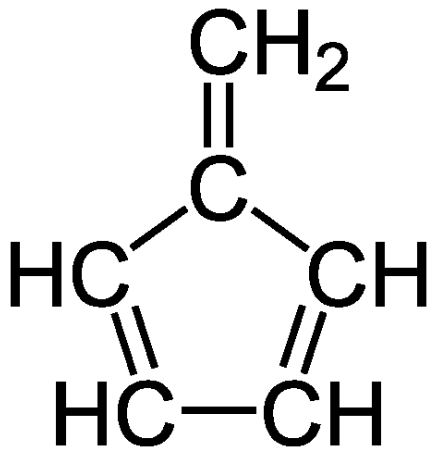
Humin substances are natural organic substances arising by decomposition of mainly plants' remains.

Humin substances are only difficult further decomposed and are contained in the Soil, Peat, Coal and some Water sources at very high Level.

Humin substances are divided according their solubility in Water to:

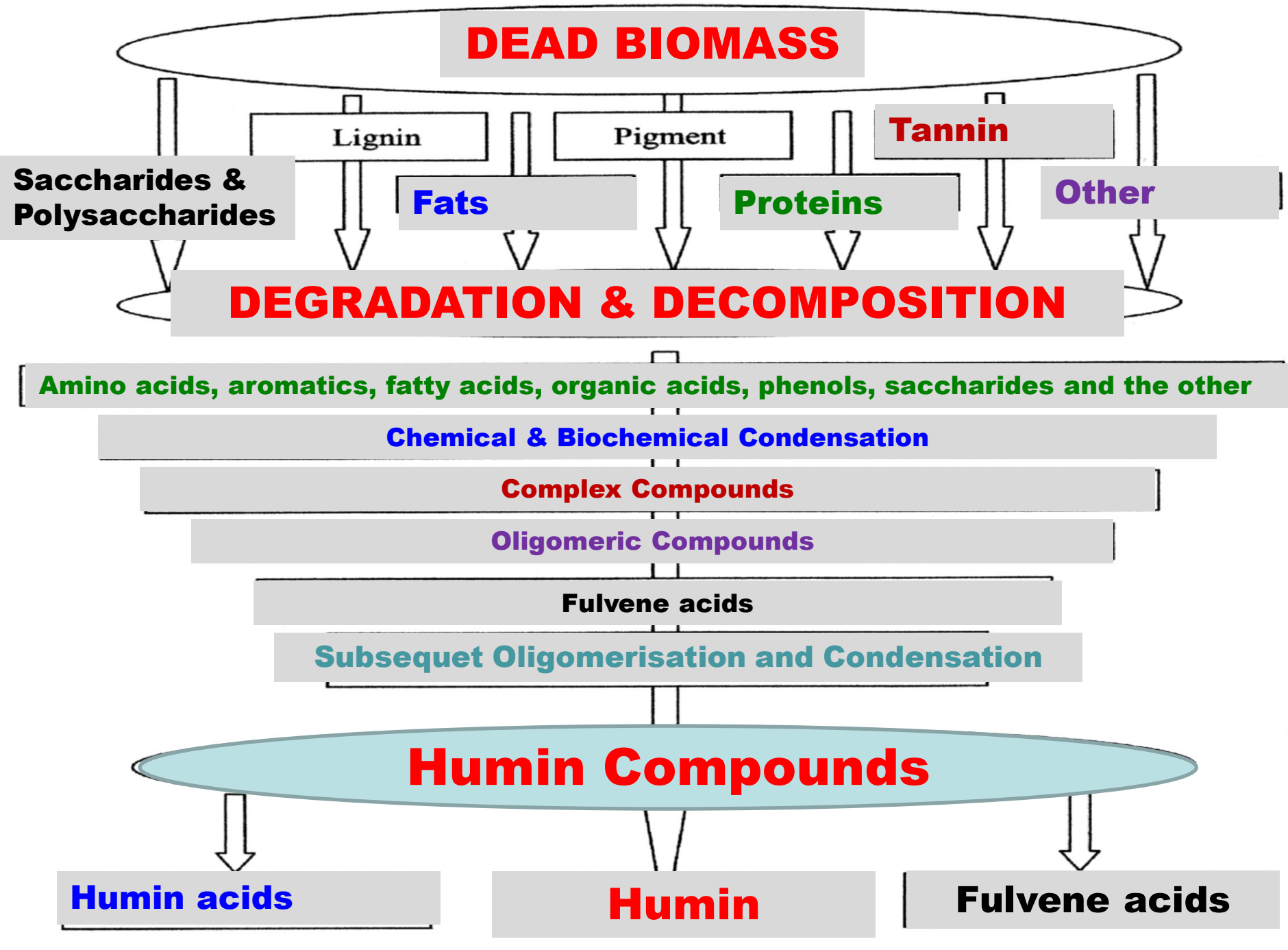
- Humins,
- Humine acids,
- Fulvene acids.

FULVENE

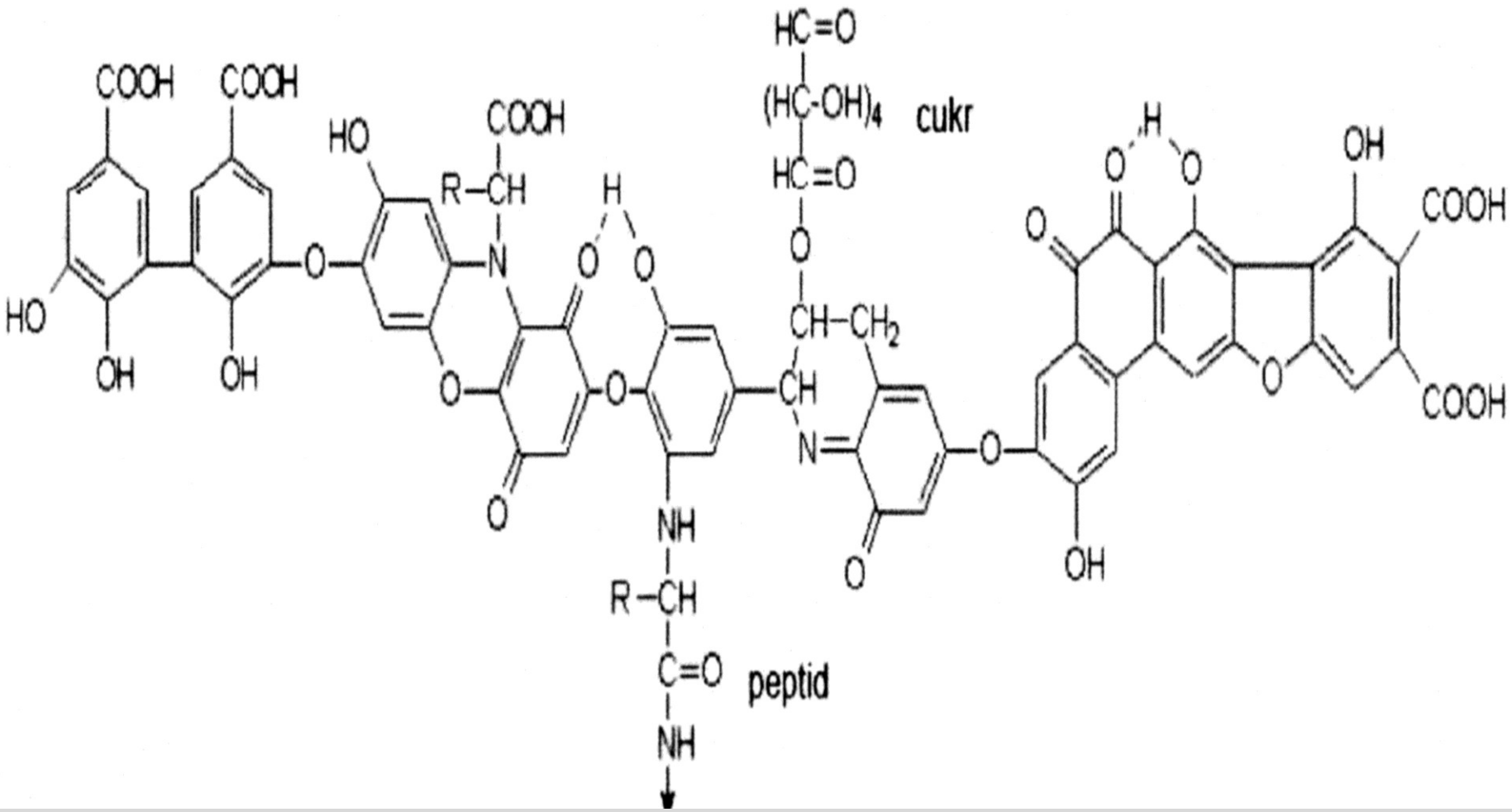


Humin Acids 1

- **Humin acids** are insoluble in Water at pH 2 and lower, but are soluble at higher pH. The Typical colour is brown to black-brown
- **Humin acids** contain –OH and –COOH groups


DEAD BIOMASS
Lignin
Pigment
Tannin
Saccharides & Polysaccharides
Fats
Proteins
Other
DEGRADATION & DECOMPOSITION
Amino acids, aromatics, fatty acids, organic acids, phenols, saccharides and the other
Chemical & Biochemical Condensation
Complex Compounds
Oligomeric Compounds
Fulvene acids
Subsequet Oligomerisation and Condensation
Humin Compounds
Humin acids
Humin
Fulvene acids

Humin Acids 2



HYPOTHETICAL FORMULA of **Humin Acids according to Stevenson (1992)**

Humin substances

- **Humin substances** are used mainly for the Plant nutrition. Although it is not a Fertilizer as it is usually meant (Material containing N, P, K), it enables easier intake of the Plant nutrition , stimulating formation of the Root system. Thank this the Plant is able to absorb better Water and nutrition. It promotes photosynthesis and improves the Soil properties.
- **Humin substances** are supplied for agriculture use as the Solution, powders or pellets. They are able to be applied as a Spray, possibly combined with the other Fertilizers or Chemicals for Plant protection.

1. Generation of the Biodegradable synthetic plastics – Brown coal Humates

I have worked with it!

EXTRACTION FROM THE BROWN COAL – it is a Part, which is not enough transformed to Coal (lower carbon content) > It was a Dry dark brown powder solid.

What was the Target:

ADDITIVATION OF THE LDPE TO PRODUCE A BIODEGRABLE FILMS