Hemicelluloses

FS630
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Outline

• Sources, characteristics and common properties
• Xylans
• Mannans
• Xyloglucans
• Mixed-linkage β–D-glucans
• Hemicellulose derivatives and their applications
Origin and Sources

Plant/wood cell:

LM: intercellular space
P: Primary wall (lignins, pectins, hemicelluloses, little cellulose)
S1
S2 Secondary wall (mainly cellulose + pectins, hemicelluloses, lignins)
S3

50% of the biomass of annual and perennial plants

Origin and Sources

Hemicellulose = polysaccharides found in cell-walls of plant that are not cellulose (polymer of β(1,4)-D-glucose) or pectins (polymer of galacturonic acid), including some gums

Great variety of hemicelluloses with various building blocks

Pentoses: xylose, arabinose
Hexoses: glucose, mannose, galactose, rhamnose (and their corresponding uronic acids)

Mainly D stereoisomer
α or β linkages
(1→4), (1→3) or (1→6) linkages
Pyranose or furanose forms for hexoses

HemicelluloseS
## Origin and Sources

### 4 main categories depending on the backbone-chain composition:

- Xylans
- Mannans
- β-glucans
- xyloglucans

Main industrial applications so far: conversion into sugars, chemicals, fuels and sources of heat energy

Applications as biopolymers not yet exploited on industrial scale

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### Extraction

- most often in hot alkali (NaOH/H₂O₂),
- sometimes in hot water (xyloglycan gums) or steam treatments

### Structural features:

- backbone chain,
- side-chain types and distribution,
- glycoside linkages types and distribution,
- Mw

### Characterization by

- HPSEC-MALLS,
- MALDI-TOF MS,
- $^{13}$C-CP/MAS NMR
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Xylans

Heteropolymers possessing a β-(1→4)-D-xylopyranose backbone

⇒ Homoxylans: true homopolymer occurring in seaweeds

\[ \beta-(1\rightarrow3)\text{-D-xylan} \]

\[ \beta-(1\rightarrow3, 1\rightarrow4)\text{-D-xylan} \]
Xylans

**Glucuronoxylans**: isolated from hardwoods

1. In the native state, xylan is supposed to be O-acylated, but the acetyl groups are split during the alkaline extraction ⇒ partial or full water-insolubility

![4-O-methyl-D-glucurono-D-xylan](image)

**Arabinoxylans**: in a variety of the main commercial cereals (wheat, rye, barley, oat, rice, corn, sorghum,...) = major hemicellulose component of flour and bran (dietary fibers).

**Complex heteroxylans**

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Xylans

**Potential resources**: by-products of forestry and pulp-and-paper industry (forest chips, wood meal and shavings), annual crops (straw, stalks, husk, hulls, bran,...)

**Extractability** restricted due to physical and/or covalent interactions with other cell-wall constituents (e.g. xylan can be ester-linked to lignin through uronic acid side-chains)
Xylans

Can be surface active agents: most xylans form oil in water emulsions with stability comparable to that of Tween 20. Low foamability.

Role in bread making: affect properties of the dough and texture/end-product quality of baked products.

Biological activity: part of dietary fibers

Potential applications:
- Polymers: “super gel” for wound dressing, micro- and nanoparticles for controlled drug delivery
- Oligosaccharides: novel functional food ingredients modifying food flavor and physicochemical characteristics: model compounds for enzymatic assays

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Mannans

Heteropolymers possessing a $\beta$-(1→4)-D-mannopyranose backbone

$\Rightarrow$ Homopolymer: rare

$\Rightarrow$ Galactomannans: abundant in cell walls of storage tissues, notably those from the endosperm of leguminous seeds (guar, locust bean, tara gum,...). The amount of galactose residues influences solubility, viscosity and interactions with other polysaccharides.

$\Rightarrow$ Glucomannans: major component of the secondary cell walls of softwoods

Interactions properties: gums from konjac, guar or locust bean affect the pasting behavior of starch (RVA method)

Biological activity: guar and konjac gums show ability to lower the level of plasma and liver cholesterol. Other mannans show immunomodulatory activities.
Mannans

Potential applications: konjac gum modify the Tg of sugar/polysaccharide mixtures ⇒ potential replacement of gelatin in sugar, hard-boiled and frozen confectionery products

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Xyloglucans

Cellulosic, i.e. \((1\rightarrow4)-\beta-D\)-glucopyranan, backbone decorated with \(\alpha-D\)-xylopyranose residues at position 6

Very tightly hydrogen-bonded to the cellulose microfibrils of the cell wall of plants ⇒ negatively affects extractability

Regularity in the distribution of side chains ⇒ 2 major types:

- **XXXG** (3 consecutive xylosylated glucopyranose residues separated by 1 unsubstituted glucopyranose residue) in cell wall of higher plants
- **XXGG**, in seeds of many plants

Xyloglucans

**Gelling ability**: used as thickening, stabilizing and gelling agent in food, textile sizing and weaving, adhesive or binding agent ⇒ XG from tamarind seed

➊ XG significantly decreases retrogradation and syneresis of starch paste

Modified tamarind seed XG can form reversible gels upon heating and cooling

**Potential application**: adhesive properties ⇒ wet-end additive in paper-making
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$\beta$-glucans

Mixed linkages (1→3, 1→4)$\beta$–D-glucans, found in cereal grains
Principal molecules associated with cellulose microfibrils during cell-growth

Interest arose because of:
• problems caused in brewing and animal feed industry
• health benefits (cholesterol reduction, regulation of postgrandial serum glucose levels, immunostimulatory activity)
β-glucans

Extraction from cereal grains more difficult than other hemicelluloses from woody tissues (removal of starch, lipids, proteins, phenolics)

Aggregates even in dilute solutions

Potential applications:
  • Accepted as functional bioactive ingredients
  • interactions with starch (reduced enthalpy of starch gelatinization, reduced swelling of starch granule)
  • Viscosity enhancing effect: thickening agent for gravies, salad dressings or ice-cream formulations; stabilization of emulsions and foams
  • Change in the perception of mouth-feel for beverages

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**Hemicellulose derivatives**

- Etherification, cationic hemicelluloses, esterification, specific C6 oxidation of guar, hydroxypropyl derivatives, carboxymethyl derivatives

- Enhanced emulsifying and protein-foams stabilizing properties; modified swelling power, solubility and tolerance to organic solvents


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**Hemicellulose derivatives**

**Case study: Xylophane AB**

1- Study of acetylation of glucuronoxylan from aspen wood

High degree of acetylation ⇄ soluble only in aprotic solvents (non-acetylated glucuronoxylan is partially soluble in hot water), lower water content, acetylation prevents thermal degradation, glass transition temperature making it possible to thermoprocess acetylated glucuronoxylan

2- Modification of the process

3- Final product

Films with efficient barrier against oxygen, grease and aroma ⇄ prolongation of shelf life food stuffs
## Summary

- Great structural diversity
- Under exploited at industrial scale (except gums)
- Great potential resources (agriculture by-products)
- Potential applications in food science