Kirk-Othmer Encyclopedia of Chemical Technology.

HEMICELLULOSE

Hemicellulose [9034-32-6] is the least utilized component of the biomass triad comprising cellulose (qv), lignin (qv), and hemicellulose. The term was originated by Schulze (1) and is used here to distinguish the noncellulosic polysaccharides of plant cell walls from those that are not part of the wall structure. Confusion arises because other hemicellulose definitions based on solvent extraction are often used in the literature (2–4). The term polyose is used in Europe to describe these noncellulosic polysaccharides from wood, whereas hemicellulose is used to describe the alkaline extracts from commercial pulps (4). The quantity of hemicellulose in different sources varies considerably as shown in Table 1.

The complex nature of hemicellulose components and their degradation products after commercial processing makes a logical system of nomenclature difficult (12). An arbitrary system of nomenclature has evolved in which source and history is included along with a generic classification based on IUPAC conventions. Thus *O*-acetyl 4-*O*-methyl-D-glucuronoxylan, arabinogalactan, etc, are generic terms in which the main components are enumerated, and the unique character of each polymer is highlighted by including a distinguishing aspect, such as aspen glucomannan, esparto xylan, or spruce kraft arabinoxylan.

Pure hemicellulose components are seldom extracted directly from their source. Extracts are a mixture of polysaccharides, lignin, and lignin-hemicellulose complexes (by chemical linkages and possibly physical interactions) (13) characteristic of their origin and the solvent employed. Hemicellulose has a lower degree of polymerization (DP) than cellulose (about 200 vs more than 10,000) and its lower limits have not been clearly defined. The extract may contain two or more polymers of similar composition but different structures (polydiversity) or of different distributions and amounts of branching or bonding in otherwise similar molecules (polydispersity) (2, 14, 15). If a single polymer is present, it may exhibit a spectrum of molecular weights (polymolecularity) which may exhibit a Gaussian or biased distribution. A pure hemicellulose component is one where polydiversity has been avoided and a degree of heterogeneity has been attained compatible with end use application.

The data in Table 2 illustrate the composition of the hydrolysates of arborescent plants. Most of the glucose comes from cellulose, and the remaining glucose and other sugars are derived chiefly from the hemicellulose components. The most common hemicellulose in angiosperms is composed of a D-xylose [58-86-6] arranged in a linear manner. D-Mannose [3458-28-4] is derived from a glucomannan which is the most common hemicellulose in most gymnosperms. Both contain other sugars and exist in a variety of configurations and molecular weights. Specialized parts such as reaction wood, branch wood, cambium, bark, rays, vessels and resin canals, etc, contain these components and other exotic polysaccharides whose exact function in the plant is not understood (see Carbohydrates; Wood). This article concentrates primarily on the components of tracheids and fibers of arborescent plants.

The common hemicellulose components of arborescent plants are listed in Table 3. Xylans, arabinogalactans, and pectic substances are common to all while only traces (if at all) of glucomannans are found in the cell walls of bamboo. Other polysaccharides are found in trace amounts in wood as well as in bark, growing tissues, and other specialized parts of trees.

Table 1. Approximate Hemicellulose Content of Selected Vegetable Materials and Their Residues

Raw material	Cellulose, %	Hemicellulose,[a] %	Lignin, %	Pectic material, %	Extractives, %	Reference
algae (green)	20–40	20–50	0	30–50	[b]	5
bast fibers	80–95	5–20	0	trace	[b]	6
grasses[c]	[d]	25.1	4.3	[d]	[d]	7
corn cobs	41	36	6	3	14	8
cornstalks	29	28	3	trace	[b]	9
wheat straw	40	29	14	trace	[b]	10
temperate hardwood	3–47	25–35	16–24	trace	2–8	11
softwood	40–44	25–29	25–31	trace	1–5	11
chemical pulps	60–80	5–15	0–10	0	0	[e]

[a] Quantity can vary according to sampling and definition employed.
[b] Present, but quantities not reported.
[c] Average composition of grasses grown in temperature zone.
[d] Not reported in reference.
[e] See Cellulose.

Table 2. Composition of Hydrolysates of Vegetable Matter[a], [b]

Component	Angiosperms	Gymnosperms
D-galactose	1 ⟶ 5	1 ⟶ 20
D-glucose	45 ⟶ 50	35 ⟶ 40
D-mannose	0 ⟶ 5	12 ⟶ 20
L-arabinose	1 ⟶ 3	2 ⟶ 5
D-xylose	18 ⟶ 25	8 ⟶ 15
uronic acids	6 ⟶ 10	3 ⟶ 6
klason lignin	16 ⟶ 25	25 ⟶ 34

[a] Percent of component.
[b] Derived from data in Ref. 11.

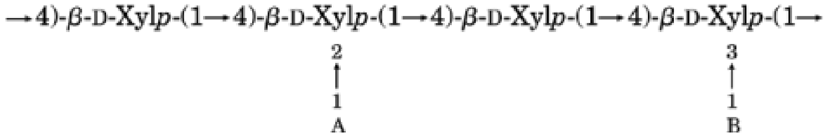
Table 3. Hemicellulose Components of Arborescent Plants

Gymnosperms	Dicotyledons	Monocotyledon (bamboo)
arabino-(4-*O*-methyl-glucurono)xylan	*O*-acetyl-(4-*O*-methyl-glucurono)xylan	arabino-(4-*O*-methyl-glucurono)xylan
O-acetylgalacto-glucomannan (0.1:1:3)	glucomannan	heteroxylans
O-acetylgalacto-glucomannan (1:1:3)	arabinogalactan	D-glucans
arabinogalactan	pectic substances	arabinogalactans
pectic substances	tension wood components	pectic substances
compression woodcomponents		

1. Structures of Hemicellulose Components

1.1. Xylans

The polymers which give rise to the sugars shown in Table 2 vary in composition and structure from species to species but can be grouped into several families. The most plentiful of these is the xylan [9014-63-5] family (Fig. 1) which is characterized by a relatively short backbone of $\beta\ (1\longrightarrow 4)$-linked D-xylopyranosyl units with 4-*O*-methyl-D-glucuronopyranosyl units attached by $\alpha\ (1\longrightarrow 2)$ bonds to some of the anhydroxylose units (11), although linkages to the C-3 position have been reported (16). The acids occur in the native state as carboxyls,



$$\rightarrow 4)\text{-}\beta\text{-D-Xyl}p\text{-}(1\rightarrow 4)\text{-}\beta\text{-D-}\underset{\substack{2\\ \uparrow\\ 1\\ \text{A}}}{\text{Xyl}p}\text{-}(1\rightarrow 4)\text{-}\beta\text{-D-Xyl}p\text{-}(1\rightarrow 4)\text{-}\beta\text{-D-}\underset{\substack{3\\ \uparrow\\ 1\\ \text{B}}}{\text{Xyl}p}\text{-}(1\rightarrow$$

Fig. 1. A schematic representation of the xylan backbone of arborescent plants, where Xyl$p$=xylopyranosyl unit; A=α -(4-O)-methyl-D-glucuronopyranosyl) unit, sometimes an acetyl; and B=α -(L-arabinofuranosy) unit, sometimes an acetyl.

esters (17), or possibly as salts. Arabinofuranosyl units, mannose, rhamnose, glucuronic acid, galacturonic acid, and *O*-acetyl groups have also been found in xylan hydrolysates and may be a component in some instances. Glycosidic and ester linkages to lignin also occur.

This polymer can be extracted in near quantitative yield from many lignified hardwoods but not from others such as elm (*Ulmus americana*) (11). The number average degree of polymerization (DP_n) of hardwood xylan varies from about 100 to 200 units depending on the source and extent of degradation during isolation. Some may possess a T or comb shape instead of a filiform structure (18). Some researchers believe the distribution of acid units on the chain is random (19); others disagree (20). A distribution of acid groups between molecules in a given extract may also occur (21). Hardwood xylans have *O*-acetyl groups on 7 out of 10 anhydroxylose units at the 2,3 position and at the 2 and 3 hydroxyl positions (22, 23). It has been shown (24, 25) that rhamnose and galacturonic acid units are part of the chain located toward the reducing end of birch wood xylan (*Betula verrucosa*). Since this terminal configuration is not present in xylans isolated from chlorite holocelluloses (26), some chlorite-labile intermediate may exist between it and the rest of the xylan molecule. Arabinose (27) and mannose units (28) are also reported in some xylan hydrolysates as terminal units. Many of the xylans of herbaceous plants and seed hairs (except for cotton which has none) are similar to those in arborescent plants (29). Removal of branch substituents from isolated xylans can result in crystallization of the residual chain (30). The xylans in other components of dicotyledons such as bark, leaf stems, etc, vary in uronic acid content and degree of polymerization from those in fibers. The greatest variation occurs in mature lateral roots of sugar maple (*Acer saccharum Marsh.*) where the main chain is composed of $\beta(1\longrightarrow4)$-linked D-glucopyranosyl and D-xylopyranosyl units (31) to which are attached branches of uronic acid and perhaps other structures.

Molecular weight studies of hardwood xylans are complicated by degradation during extraction (32) and conflicting theoretical considerations (33, 34). Although hardwood xylan is polydisperse, its polymolecularity is very low (11) and shows a maximum at $DP_n = 200$. Other studies show solutions of xylan in water (35) and aqueous dimethyl sulfoxide (DMSO) (36), unlike the acetate dissolved in organic solvents (32), undergo changes in molecular associations with time and temperature. Branching inhibits the sorption of xylan from water and alkaline solutions onto cellulosic surfaces (37).

Xylan is plentiful in and easily extracted from monocotyledons. Its composition depends on the species involved and the fraction examined (3) and has a greater degree of polymolecularity, polydiversity, and polydispersity than wood xylan (14, 38). Features of softwood xylans have been found in some xylans from bamboo (*Bambusa sp.*) (39), but most other fractions from stems and leaves are more complex (40). The DP_n of many nonarborescent monocotyledon xylans is generally lower than that found in wood, but it increases as the tissue matures (41, 42). These complex xylans are referred to as heteroxylans and their composition and DP in the stalk differs from that in the leaves (43). Sorghum husk xylan (*Syrian granum*) is composed of three such polymers of varying composition and degrees of branching (44), the ratios of which can change with plant growth (45). Rice bran (*Oryza sativa*) (45) and wheat bran (*Tritium aestivum L.*) (46) yield a heteroxylan which contains more double-substituted xylose units and more complicated branches than are found in the polymer from the endosperm (47).

Table 4. A Comparison of Isolated Xylans from Different Sources

	Relative amounts of components in hydrolysate (xylose = 10)								
Source	Gal[a]	Glc[b]	Man[c]	Ara[d]	Rha[e]	GlcA[f]	MGlcA[g]	GalA[h]	Ref.
kenaf, *Hibiscus cannabinus*	0.2	0.07	0.02	0.02	0.07	0	1.4	0	28
birch, *Betula papyrifera*	0.02	0.4	0.07	0.2	trace	0	1.2	+	11
sorghum husk	0.5	5.5	trace	7.5	trace	0	1.5	–	44
esparto grass, *Stipa tenacissima*	0.5	0.9	0.05	1.4	trace	0	0	0	46
tobacco ECP,[i] *Nicotiana tabacum*	0.2	0.3	0.1	0.4	trace	2	0	0	52
softwood, average	trace	trace	0	1.3	trace	0	2	+	11
sapote gum, exudate from *Sapota achras*	0	0	0	4.5	0	1.7	1.8	0	53

[a] Galactose.
[b] Glucose.
[c] Mannose.
[d] Arabinose.
[e] Rhamnose.
[f] Glucuronic acid.
[g] 4-*O*-Methyl-D-glucuronic acid.
[h] Galacturonic acid.
[i] Extracellular polysaccharide from culture medium.

The xylan of gymnosperms is best isolated from holocellulose. It differs from that of dicotyledons by having a greater solubility in water, no acetyl substituents, a lower molecular weight (but of uncertain magnitude), greater substitution by L-arabinofuranosyl and 4-*O*-methyl-D-glucuronopyranosyl units (11), and a different distribution of branches along the chain. Uronic acids linked $1 \longrightarrow 3$ to xylose have been reported occasionally (48), but most are linked by $\alpha(1 \longrightarrow 2)$ bonds. There is random distribution of arabinofuranosyl units along the chain (49) and the distribution of uronic acids in softwood xylans often occurs in pairs. The isolation of two electrophoretically distinct xylans from slash pine (*Pinus elliottii Engelm.*) of identical chemical composition and structure suggests that the block formation of these xylans is dissimilar (50). Like hardwood xylans, many softwood xylans are terminated at the reducing end by rhamnose units and galacturonic acid (51).

The 4-*O*-methyl-D-glucuronoarabinoxylan in other parts of conifers differs slightly in composition and in quantity from that of tracheids. The gymnosperm *Gingko biloba L.* contains a polymer almost identical to that isolated from conifers (54). A softwood-like xylan is present in the primitive cinnamon fern (*Osmundia cinnamomea*) (55). The data in Table 4 illustrate the compositions of xylans from different sources. The molecular weight of undegraded softwood xylan is not known. A polymer isolated from Norway spruce (*Picea abies (L.) Karst.*) has many long branches, is probably degraded, and the DP_n of 128 is shifted toward the high end of the distribution spectrum (56).

The amount of softwood xylan sorbed from alkali at kraft cooking temperatures (100–170°C) is proportional to the quantity of hemicellulose present and inversely to the extent of branching (57). At neutral pH, the presence of carboxyl groups inhibits sorption compared to a control, but no difference is observed when ionization is suppressed (58).

1.2. Glucomannans

Glucomannans [11078-31-2] are found in growing tissues as well as in the mature cells of many plants. They contain a chain of $\beta(1 \longrightarrow 4)$-linked D-mannopyranosyl units (11) and D-glucopyranosyl units; the latter

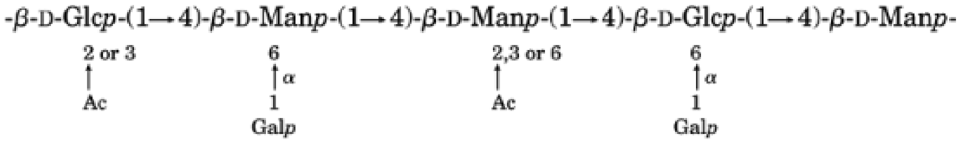


Fig. 2. A simplified schematic representation of glucomannan, where Glc*p* is the D-glucopyranosyl unit; Man*p* is the D-mannopyranosyl unit; Gal*p* is the D-galactopyranosyl unit; and Ac is the acetyl group.

Table 5. Comparison of Glucomannan Compositions from Various Sources

	Ratio of components in hydrolysate to glucose (=1.0)				
Source	Galactose	Mannose	Xylose	$[\alpha]_D$	Ref.
red maple	0	1.3		−31	11
aspen bark	0.5	1.3	trace	+10	63
red clover	0.25	1.1		−8.9	64
tobacco leaf midrib	0.5	2	0.5	−2	65
Engelmann spruce	1	3			66
	0.2	3			
ginkgo wood	1.0	1.7	0	−7	67
	0.2	3.6		−36	

is randomly distributed in the case of spruce (*Picea mariana (Mill.) B.S.P.*) (59) (Fig. 2). The polymer is chiefly located in the secondary wall of fibers (60) and is often bonded to lignin (61). It undergoes noncovalent chain–chain aggregations with other polysaccharides (62). The principal variations in composition between species of plants are the ratio of components, the presence of acetyl groups, and the occurrence of terminal D-galactopyranosyl units.

Glucomannans in dicotyledon fibers are resistant to extraction even from holocellulose and consist of a short chain of glucose and mannose building blocks devoid of branches. Most glucomannans have a ratio of glucose to mannose (Glc/Man) of 1/1.5 to 2 (11) which represents a natural variation (Table 5). Those with a Glc/Man ratio of less than unity (68, 69) may be contaminated with glucan. The isolation of a glucomannan in trace amounts by direct aqueous extraction of sugar maple wood (*Acer saccharum Marsh.*) with a ratio of components of Glc/Man = 1/4.6 illustrates the great variation in composition occurring in many natural products (70). Both glucose and mannose have been reported as nonreducing terminal groups. Galactoglucomannans are present in aspen bark (*Populus-tremuloides Michx.*) (63), clover (*Trifolium sp.*) (64), in the midrib of tobacco leaves, and in cultured cells of tobacco (65, 71), and have Glc/Man ratios characteristic of dicotyledons with the addition of terminal D-galactopyranosyl units attached to C-6 of the main chain.

Only traces of mannose occur in the hydrolysates of some monocotyledon stems (7, 9) although glucomannans occur in the tubers and leaves of some monocotyledon species (72).

In gymnosperms, Dglucose and D-mannose components are linked by $\beta(1 \longrightarrow 4)$ glycosidic bonds into a linear chain to which galactose units are attached by $\alpha(1 \longrightarrow 6)$ glycosidic bonds (11). It is the primary hemicellulose component of the normal cell wall of most, but not all (73), conifers and in the native state contains *O*-acetyl units (74). Polydiversity is seen in the widely varying galactose content. The galactose-deficient galactoglucomannan (0.1:1:3) of conifers displays a relatively constant composition from source and species to species. Glc/Man ratios mostly range from 1:3 to 1:4 (11, 75) and the slight variation observed in galactose content is probably within experimental error. The galactose content of the galactose-rich galactoglucomannans (1:1:3) exhibits a much greater variation from 11 to 27% (76–78). In some instances, polymers containing about 10% galactose content (0.5:1:3) can be fractionated further (75). Greater deviations in composition are reported for small fractions from Engelmann spruce (*Picea engelmannii Parry*) (79), Norway spruce (*Picea abies (L.)*

Karst.) (80), and black spruce (75). It is possible that galactose to galactose linkages also exist in one fraction from Engelmann spruce (79).

The presence of galactose units increases the solubility of the polymer in water as well as that of its various derivatives in their appropriate solvents (11, 80, 81), allowing some to be extracted directly from milled wood (77). Acetyl groups such as galactose branches also confer solubility in water and DMSO (82–84). The naturally occurring acetyl groups are located along the chain in a random manner (85) on the C-2 and C-3 positions of the anhydromannose units of the polymer from pine (86) and on the C-3 position of both glucose and mannose in the case of Parana pine (*Auraucaria angustifolia*) (84). Substitution at C-6 occurs in pine (*Pinus densiflora S. and Z.*) as well as at C-2 and C-3 (87).

Very little galactose-rich polymer can be isolated from coniferous bark, although a water-soluble component with a lesser galactose ratio was isolated (88–90). The bark of Lodgepole pine (*Pinus contorta Dougl.*) and Ginkgo xylem (as well as the shell of Ginkgo nut (90)) yields glucomannan extracts rich in glucose (91). Ray cells of normal red pine wood (*Pinus resinosa Ait.*) contain smaller amounts of galactose-rich glucomannan than tracheids. Both types of galactoglucomannans are claimed to be present in the cambium tissues of jack pine (*Pinus banksiana Lamb.*) before lignification takes place (92). The wide range of galactoglucomannan compositions from various sources is illustrated in Table 5.

The molecular weight of glucomannans is not as great as that of hardwood xylan (11), and when isolated from the same source can have different ratios of number to weight average molecular weights; being a Flory distribution in one instance (93) and not in another (94). No correlation exists between the viscosity of red pine (*Pinus resinosa Ait.*) glucomannan fractions, and their DP (95), and may reflect linking between lignin and glucomannan (60). The sorption of a ^{14}C-labeled white spruce (*Picea glauca (Moench) Voss*) glucomannan onto cellulose from water at temperatures from 5 to 40°C was found to occur more rapidly than a tritium-labeled birch xylan (96). The apparent Arrhenius activation energy from initial sorption rates was 27.6 kJ/mol (6.6 kcal/mol) for the former and 41.8 kJ/mol (10 kcal/mol) for the latter. A galactoglucomannan (0.2:1:3) exhibited monolayer deposition onto a cellulose substrate from water when acetyl groups were present and multilayer deposition when deacetylated (97).

1.3. Galactans

Hemicellulose galactans are found in the reaction wood of dicotyledons and gymnosperms. The tension wood of beech (*Fagus sp.*) contains a polymer composed of D-galactose, L-rhamnose, L-arabinose [328-37-0] and D-xylose in the ratio of 62.4:22.2:9.7:5.7 (98). Galactopyranosyl units constitute the main chain; the other sugars as well as some galactose occur in the branches. Galacturonic acid and 4-*O*-methyl-D-glucuronic acid are also present. Identified fragments from partial acid hydrolysis resemble those from the gum of *Combretum leonense* (99). The degree of polymerization of 344 is much less than that of the gum and is skewed toward low molecular weight species. A less complicated, possibly linear $\beta(1{\longrightarrow}3)$-linked galactan has been found in *Rosa glauca* cells grown *in vitro* (100).

A polysaccharide is present in coniferous compression wood having a slightly branched main chain of $(1{\longrightarrow}4)$-linked β-D-galactopyranose residues with single-terminal β-D-galacturonic acid residues attached to C-6 of the main chain (101). It is best isolated from the chlorite liquor of holocellulose preparations of the compression wood of red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), and tamarack (*Larix larcianan*). It is also found in the ray cells of normal and compression wood.

1.4. Glucans

It has been shown (102, 103) that the secondary phloem and ray cells of Scots pine (*Pinus sylvestris L.*) as well as many coniferous compression woods (101), contain a $(1{\longrightarrow}3)$-linked glucan (named laricinan) with a degree of polymerization of 174 to 205 (104). Its composition and insolubility after isolation resembles that of curdlan, but structural differences may exist. About 6 to 7% $(1\longrightarrow 4)$ linkages and traces of glucuronic and galacturonic acids are also present in the main chain as well as about eight branch points per average molecule.

Monocotyledon cell walls contain polysaccharides composed of a mixture of β-$(1\longrightarrow 3)$- and $\beta(1\longrightarrow 4)$-linked glucopyranosyl residues which are commonly referred to as β-D-glucans (105). Only a few $(1\longrightarrow 3)$ linkages are present in this polymer and uronic acids have not been reported to be present. It is a significant hemicellulose component in bamboo stems and leaves (36)and constitutes up to 75% of the cell wall of barley (*Hordeum distichum L.*) endosperm (106). The sequencing of the linkages in the latter polymer indicates few contiguous $\beta(1\longrightarrow 3)$ linkages are present. The insertion of irregularly spaced $\beta(1\longrightarrow 3)$ linkages in a predominantly $\beta(1\longrightarrow 4)$-linked structure loosens the otherwise rigid structure and allows it to assume a worm-like configuration (107).

1.5. Xyloglucans

These polysaccharides occur in trace amounts in tracheids and fibers of arborescent plants and in larger quantities in forage plants (7). They are also found in the cambial tissues of dicotyledons (108) and gymnosperms (66), the cultured cell walls of gymnosperms (109) and primary walls of cultured angiosperms cells (105), as well as the medium in which the cells were grown (110, 111). Its sources, structures, and functions have been reviewed (112). They are similar in many respects to amyloid, a reserve carbohydrate in many seeds (113), but they possess additional components. Both polysaccharides give a characteristic blue-green color with iodine. The polymer consists of a cellulose-like backbone with D-xylosyl side chains linked by $\alpha(1\longrightarrow 6)$ bonds to many of the glucosyl residues (114). There are many variations of this basic structure such as the presence of acetyl groups and terminal D-galactose, L-rhamnose, L-arabinose, and L-fucose units (114). The polymer has been detected in the cambial tissues of pine (*Pinus banksiana Lamb.*) (92), identified in aspen (*Populus tremuloides*) and linden (*Tilia americana L.*) cambial tissues (103), but has not been detected in the mature (one-year-old) tracheids of pine (92) suggesting it is a transient component of the primary wall which disappears on maturation.

The xyloglucan found in tamarind seeds has a greater molecular weight than that found in the cell walls but it does not contain L-fucose, acetyl, or pyruvyl substituents. The latter probably plays a unique role in the development and growth of plants (112, 115). Xyloglucan is polydisperse, the number-average molecular weight of the polymer from the cambium tissues of poplar and linden is 62,000 Daltons, and the distribution shows a pronounced left-hand skewness (108). A similar distribution was found for tamarind amyloid although the molecular weight was much greater $(1.4 \times 10^6 \text{ Daltons})$ (116).

Both types of xyloglucans exhibit monolayer sorption onto cellulose (116) and tamarind xyloglucan exhibits maximum specific sorption onto cellulose less than that of coniferous xylan. By inference with other data, this is also less than that of glucomannan and hardwood xylan, but similar to many additives used in the paper industry.

1.6. Pectic Substances

Polymers rich in D-galacturonic acid have been isolated from pollen, fruit, seeds, bark, stalk, roots, aquatic plants, exudates, cultured tissue, and the media in which it is grown. They are not considered to be hemicellulose by some definitions (2), but many are cell wall components. Because of their susceptibility to degradation by enzymes, acids, alkalies, and oxidants during aging and isolation, research has concentrated on accessible polymers from cultured plant tissues (117). True pectins are characterized by the presence of an *O*-(α-D-galacturonopyranosyl)-$(1\longrightarrow 2)$-L-rhamnopyranosyl linkage within the molecule but it is absent in many other pectin-like substances. At one extreme are simple galacturonans (118–120), whereas at the other is rhamnogalacturonan II which contains at least 10 different monosaccharide components, some unique to pectin, in the main chain or as a component of branches (121). Pectins of intermediate complexity contain alternate rhamnose and galacturonic acid units and are found in certain roots (122); others have branches of glucuronic acid linked to galacturonic acid. Rhamnogalacturonan I is most plentiful in the cell walls of cultured sycamore tissue (*Acer pseudoplatanus L.*) and has complex branches attached to half of the rhamnopyranosyl units (117). Acetyl and methoxyl groups are present in amounts which often vary with the state of development of the plant.

A rationalization of the complex behavior of pectins in solutions and gels with respect to their structure, solvation, and the presence of ions and other saccharides has been presented (123). The solution and sorption properties of gum tragacanth and the pectin isolated from the roots of *Hibiscus manihot L. (Tororoaoi)* contributes to their use in specialty paper manufacture (124–126).

1.7. Arabinan

This highly soluble polymer is found in the extracts of many fruits and seeds, in the boiling water extracts of pine wood (127), in the extracts of marshmallow roots (*Althaea officinalis*) (128), and aspen (63) and willow (*Salix alba L.*) (129) bark. Because arabinan can be isolated from mildly degraded pectin fractions, it is often difficult to determine whether it is a hemicellulose or a labile fragment of a larger polysaccharide and/or lignin complex. Arabinans have a complex structure composed almost entirely of 5-linked α-L-arabinofuranosyl units with similar residues linked to them at C-2 and/or C-3 and is soluble in 70% aqueous methanol solution.

1.8. Arabinogalactans

Arabinogalactan [9036-66-2] is found in association with proteins (as components of proteoglycans and glycoproteins) and free of such associations (130, 131). It occurs in cell walls of plants and as an exudate in the pores and lumens of larch tracheids. The water-soluble extracts of Western (*Larix occidentalis Null.*) and Siberian (*L. sibirica*) larch heartwood are especially rich in this polymer. Although it is not a hemicellulose, its structure has been well investigated because of its availability (up to 20% of the heartwood), economic potential, detrimental effects on pulping processes, and because it probably resembles that polymer found in the cell wall very closely. Larch arabinogalactan is composed of two easily separated fractions (molecular weights 10,000 and 16,000) in which the ratio of galactose to arabinose is about 6:1. The polymer is highly branched with $\beta(1, 3)$ and $\beta(1, 6)$ linkages between D-galactose units (11). Research suggests that the main chain of the polymer from larch (like that of some Acacia gums) consists of blocks of about 12 D-galactopyranosyl units joined by $(1 \longrightarrow 6)$ bonds which provide considerable flexibility to the molecule. Branches are composed of $(1 \longrightarrow 6)$ linked galactopyranosyl units and 3- or 5-linked arabinofuranosyl residues terminated by galactose or arabinose. Glucuronic acid is a component of the arabinogalactan of many other conifers except Western larch. No clear line of structural demarcation exists between those coniferous arabinogalactans and exudates such as Acacia gums (120).

1.9. Glucuronomannans

Most glucuronomannans occur as components of certain plant gums and are characterized by the presence of an *O*-(β-D-glucurono-pyranosyl)-$(1 \longrightarrow 2)$-D-mannopyranosyl linkage in the molecule (65). Less complex glucuronomannans are found in the tissues of bracken (*Pteridium aquilinum*) and in tobacco leaf cells where they may be part of the cultured cell wall (132) and exude into the medium in which the cells are grown (133).

2. Isolation and Analysis

Techniques for the isolation of hemicellulose depend on the intended end use and whether it occurs in soluble waste material or is part of a solid matrix. Isolation is more difficult from solids as diminution of particle size and removal of undesired encrustants such as lignin is necessary to increase accessibility and destroy lignin–hemicellulose bonds (13). Delignification techniques, except for those using ethanolamine, employ oxidants. Peroxides, peroxyacetic acid (134), and chlorine dioxide (1) have been used but the most common reagents are chlorine and acidified sodium chlorite (135). The former reagent is the least degradative (134), but it does not lend itself readily to large-scale preparations. The latter method requires less attention during preparation, can be conducted safely on a large scale, and can be manipulated to obviate the need for attrition (136).

Delignification extracts varying amounts of hemicellulose. Low reaction temperatures and (where possible) high salt concentrations minimize losses and concomitant chemical degradations such as oxidation and the effects of pH. Pectic substances and easily soluble arabinans, arabinogalactans, galactoglucomannans, xylans, and compression wood galactans are found in waste chlorite liquors (136, 137). Carbonyl groups (excepting carboxyls) are frequently reduced with a suitable reagent before alkaline extractions are attempted to minimize β-elimination reactions (134). The use of an inert atmosphere during alkaline extraction prevents oxidation by oxygen.

Extraction of hemicellulose is a complex process that alters or degrades hemicellulose in some manner (11, 138). Alkaline reagents that break hydrogen bonds are the most effective solvents but they de-esterify and initiate β-elimination reactions. Polar solvents such as DMSO and dimethylformamide are more specific and are used to extract partially acetylated polymers from milled wood or holocellulose (11, 139). Solvent mixtures of increasing solvent power are employed in a sequential manner (138) and advantage is taken of the different behavior of various alkalies and alkaline complexes under different experimental conditions of extraction, concentration, and temperature (4, 140). Some sequences for these elaborate extraction schemes have been summarized (138, 139) and an experimenter should optimize them for the material involved and the desired end product (102).

The separation of the polysaccharide components utilizes their different solubilities, polar groups, extents of branching, molecular weights, and molecular flexibilities and may be accomplished batchwise or with easily automated column techniques such as column or high performance liquid chromatography. These procedures have been summarized in several reviews (3, 141–143).

The increasing sophistication of analytical techniques coupled with suitable fractionation procedures has made the heterogeneity of hemicellulose components increasingly apparent (142). These techniques common to polymer chemistry include gas chromatography–mass spectroscopy, and proton and ^{13}C-nuclear magnetic resonance spectroscopy (144). Advances in functional group analysis and techniques for configurational and molecular studies (especially on the microscale) are frequent and the subject of numerous reviews (145). Molecular studies employ viscometry, osmometry, x-ray techniques, light scattering, and chromatographic and centrifugal techniques (11, 146), as well as the use of optical rotatory dispersion and circular dichroism (4, 140–146).

3. Pulping

The complex behavior of hemicellulose during pulping has been reviewed (147). When hemicellulose and lignin dissolve with the help of chemical transformations, fresh cellulosic surfaces are created and competition for deposition in these spaces arises between the dissolved components (148–150). Hemicellulose degradations also occur and are related to pH (acid hydrolysis, β-elimination reactions, redox reactions, etc (147)), and pyrolytic effects (151) to an extent dependent upon the time, temperature, and liquor composition of the cook (147, 152). These reactions are rendered more complex because the cell wall controls the diffusion of the reactants and products into and out of the fiber so that hemicellulose may not be able to react or diffuse out of the fiber before the cook is completed. Under pulping conditions, the formation and cleavage of lignin–hemicellulose bonds (147) and possible carbohydrate–carbohydrate bonds (153) occurs complicating the nature of the product. The extent to which these competing reactions is accomplished is reflected in product composition and end use quality and is the subject of much empirical research (152).

Alkaline (kraft) processes are much more amenable to kinetic studies than acidic (sulfite) processes. After an initial rapid loss of easily soluble and accessible polysaccharides and lignin, hemicellulose losses proceed at a slower apparent first-order rate (154, 155), dependent upon the temperature, time, and pH (liquor composition). Because of the changing nature of hemicellulose, the solubility and sorption characteristics are changed (156). Model experiments show isolated hemicellulose components behave in a similar manner and are influenced by the nature of the glycosidic bonds and the type of branching (157–162). Hydrolysis of kraft pulps at different yields shows the losses of lignin, and sugars (except mannose) proceed in a manner proportional to yield loss throughout the cook (154, 163). Mannose losses from softwoods are greatest in the 80 to 90% pulp yield range and then become very resistant to removal. The quantity of hemicellulose remaining in pulp after processing is shown in Table 1. Those pulps with about 15% hemicellulose are usually used for paper manufacture, whereas those with 5% or less are used where a high cellulose content is required. The proportion of glucomannan is slightly greater in sulfite pulps, whereas the quantity of xylan is somewhat greater in kraft and soda pulps. These proportions can be altered slightly by changes in the cooking schedule.

Suitable pretreatment of wood before pulping alters this behavior of hemicellulose significantly. Saponification of the acetyl groups of softwood before sulfite cooking results in glucomannan retention in the final product (163, 164). Those treatments that limit the peeling reaction during alkaline pulping processes (reductions with $NaBH_4$, H_2S, or oxidations with chlorite, polysulfide, anthraquinone, etc), can result in polysaccharide retention (165). The pretreatment of wood with mineral acid or liberated acids of wood at elevated temperatures (ie, 170°C for 30 min) diminishes the DP of hemicellulose components sufficiently that they will be consumed mostly during a subsequent alkaline cook (166). The resulting pulp behaves more like cotton cellulose in many industrial applications.

Figure 3 illustrates the transformations hemicellulose undergoes during commercial pulping operations as a result of acid hydrolysis or the many degradations induced by alkaline reagents. The changes shown are those that would occur if all were brought to completion after removal of most of the lignin, after washing with water, and before the pulps have undergone bleaching (147). Separation of these new compounds is best accomplished after destruction of lignin–carbohydrate bonds and the removal of lignin. Miscellaneous, labile, and accessible soluble polysaccarides are removed under these pulping conditions but they may be present together with incompletely transformed hemicellulose in high yield pulps. The hemicellulose components of hardwoods and bamboo follow the same pattern.

4. The Effect of Hemicellulose in Commercial Products

Hemicellulose components have an effect on the properties of products in which they are present. In the case of viscose manufacture much of the hemicellulose which remains in the product has only a marginal effect on strength properties and brightness and no effect on heat stability (167). It does contribute to swelling in yarn, and that remaining in the spent viscose liquor is harmful to filter presses. Increased clogging of spinnerets, low color index, and decreased yarn strength can also result when resin, cations, and hemicellulose are together in the steeping liquor (168).

When uronic acid and L-arabinofuranosyl branches are lost as a result of processing, the poor solubility of xylan acetate in organic solvents contributes adversely to cellulose acetate processing (169, 170). The haze density (opaqueness) of solutions and solid products increases as hemicellulose components become less branched. Glucomannan in an acetate product contributes less haze than xylans but more than arabinoxylans. It is responsible for the false viscosity of cellulose acetate solutions derived from wood pulp. Glucomannan also causes filtration difficulties during processing, but the effects of xylans are unpredictable.

An understanding of the effect of hemicellulose on paper products is less clear because the formation of paper webs largely depends on their structure, which is influenced by many factors besides hemicellulose (171). Arabinogalactans, which are not sorbed onto cellulose, do not have an influence (172), whereas xylans and

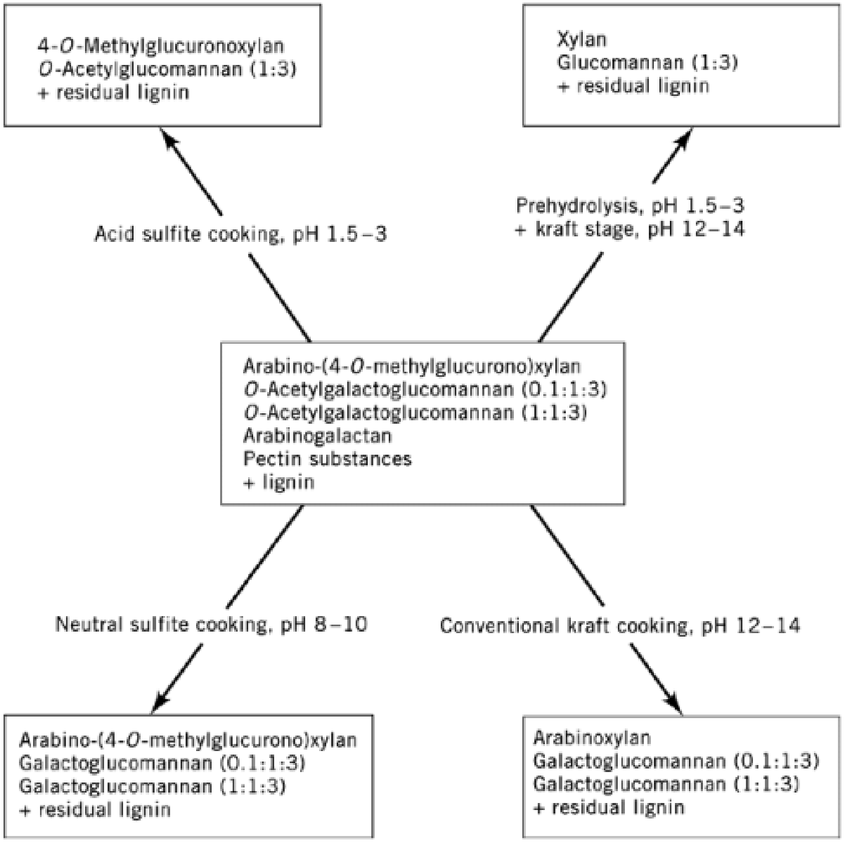


Fig. 3. The changes in coniferous hemicellulose as a result of pulping processes and before bleaching.

glucomannans and their survivors from the pulping processes do have an influence (173). The highly branched xyloglucan is sorbed but does little to improve the results of paper tests (116). Hemicellulose and related gums and mucilages help maintain a random dispersion of fibers in the furnish which results in more uniform and mechanically stronger paper webs. It also increases the rate at which pulp fibers respond to mechanical action (beating) and increases fiber bonding. The strong interfiber bonds formed after drying can alter paper structure and lead to losses in tearing strength and decreases in opacity if they are too extensive (171).

It has been proposed that differences in the tearing strengths of sulfite and kraft pulps are due to differences in the location of hemicelluloses in fiber walls (174). Other experiments suggest the location of hemicellulose in fiber walls does have an influence on tearing strength but not on tensile strength (175). A correlation of retained hemicellulose and operational variables during pulping processes has been carefully examined (176), but theoretical relationships between the parameters have not been established.

5. Applications

Hemicellulose and hemicellulose-like polysaccharides are beneficial components of foodstuffs because of their interactions between water and water-insoluble components (177). Endogenous polysaccharides are responsible for processing characteristics as well as texture and mouthfeel. Other properties such as gel formation, swelling of dough, fermentation, and optical properties are achieved using suitable treatments with enzymes and chemicals. Hemicellulose in spent liquor is mostly destroyed during modern alkaline pulping processes, and the residual fragments, unlike lignin, do not contribute greatly to the energy requirements for chemical recovery.

Hemicellulose constitutes a large reserve of raw material which can be converted to many products by chemical and biochemical means. Besides its inherent usefulness as a naturally occurring component of some manufactured products, it can be utilized either as a polymer or as the source of chemical intermediates. The former use is complicated since the mixture of polysaccharides and lignin in extracts requires special treatment if one component is to be isolated. The complexity of most hemicellulose extracts complicates the choice of use. As a result, the naturally occurring gums and mucilages are at a competitive advantage in the marketplace (178–180).

Larch arabinogalactan is easy to isolate and requires limited purification for many uses (181). The mixture of sugars, oligosaccharides, degraded hemicellulose, and lignin found in the liquors and condensates from Asplund-like and prehydrolysis pulping processes is used for binding and extending animal fodder. The sugars and oligosaccharides in waste sulfite liquor can be used for furfural production and the growth of yeast but no sugars survive in liquors from the predominant kraft processes. The quantities of xylan available for utilization greatly exceeds the quantity of arabinogalactan but its diverse nature complicates such use and the accumulation of the biomass necessary is expensive. Pectin is used in the food industry (182), and apart from specialty uses finds limited application in the paper industry (183).

Derivatives of hemicellulose components have properties similar to the cellulosic equivalents but modified by the effects of their lower molecular weight, more extensive branching, labile constituents, and more heterogeneous nature. Acetates, ethers, carboxymethylxylan (184), and xylan–poly(sodium acrylate) (185) have been prepared.

Reviews of the chemicals that can be derived from hemicellulose and arabinogalactan have been published (178–181). The xylan family has the greatest potential because of its widespread distribution. Furfural [98-01-1] is obtained from pentose by strong acid treatments but changes in pulping processes and farming practices make the collection of a suitable waste difficult. Xylose, xylitol, tartaric, and trioxyglutaric acids, methanol, butanol, and 2,3-butanediol can be manufactured on a large scale but only xylose [25990-60-7] and xylitol [87-99-0] have achieved temporary economic viability. There is little demand for mannose and mannose-derived chemicals because more convenient sources than softwoods exist. Nevertheless, several schemes have been developed to provide sweeteners, humectants, and unique compounds for starting chemical syntheses if market conditions improve.

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