Fig. 4.11. Schematic representation of the hollow cylinder formed by β-cyclodextrin

The β-cyclodextrin molecule is a cylinder (Fig. 4.11) which has a primary hydroxyl (C6) rim on one side and a secondary hydroxyl (C2, C3) rim on the other. The surfaces made of pyranose rings are hydrophobic. Indeed, the water of hydration is very easily displaced from this hydrophobic cavity by sterically suitable apolar compounds, which are masked in this way. In food processing, β-cyclodextrin is therefore a suitable agent for stabilizing lipophilic vitamins and aroma substances and for neutralizing the taste of bitter substances.

4.4 Polysaccharides

4.4.1 Classification, Structure

Polysaccharides, like oligosaccharides, consist of monosaccharides bound to each other by glycosidic linkages. Their acidic hydrolysis yields monosaccharides. Partial chemical and enzymatic hydrolysis, in addition to total hydrolysis, are of importance for structural elucidation. Enzymatic hydrolysis provides oligosaccharides, the analysis of which elucidates monosaccharide sequences and the positions and types of linkages. Polysaccharides (glycans) can consist of one type of sugar structural unit (homoglycans) or of several types of sugar units (heteroglycans). The monosaccharides may be joined in a linear pattern (as in cellulose and amylose) or in a branched fashion (amylpectin, glycogen, guaran). The frequency of branching sites and the length of side chains can vary greatly (glycogen, guaran). The monosaccharide residue sequence may be periodic, one period containing one or several alternating structural units (cellulose, amylose or hyaluronic acid), the sequence may contain shorter or longer segments with periodically arranged residues separated by nonperiodic segments (alginate, carrageenans, pectin), or the sequence may be nonperiodic all along the chain (as in the case of carbohydrate components in glycoproteins).

4.4.2 Conformation

The monosaccharide structural unit conformation and the positions and types of linkages in the chain determine the chain conformation of a polysaccharide. In addition to irregular conformations, regular conformations are known which reflect the presence of at least a partial periodic sequence in the chain. Some typical conformations will be explained in the following discussion, with examples of glucans and some other polysaccharides.

4.4.2.1 Extended or Stretched, Ribbon-Type Conformation

This conformation is typical for 1,4-linked β-D-glucopyranosyl residues (Fig. 4.12 a), as occur, for instance, in cellulose fibers:

\[
\text{(4.125)}
\]

This formula shows that the stretched chain conformation is due to a zigzag geometry of monomer linkages involving oxygen bridging. The chain may be somewhat shortened or compressed to enable formation of H-bonds between neighboring residues and thus contribute to conformational stabilization. In the ribbon-type, stretched conformation, with the number of monomers in turn denoted as \( n \) and the pitch (advancement) in the axial direction per monomer unit as \( h \), the range of \( n \) is from 2 to \( ±4 \), while \( h \) is the length of a monomer unit. Thus, the chain given in Fig. 4.12 a has \( n = -2.55 \) and \( h = 5.13 \text{ Å} \).

A strongly pleated, ribbon-type conformation might also occur, as shown by a segment of
Ca$^{2+}$ ions can be involved to stabilize the conformation. In this case, two alginate chains are assembled in a conformation which resembles an egg box (egg box type of conformation):

\[
\text{Ca} \quad \text{Ca} \quad \text{Ca} \quad \text{Ca}
\]

(4.128)

It should be emphasized that in all examples the linear, ribbon-type conformation has a zigzag geometry as a common feature.

### 4.4.2.2 Hollow Helix-Type Conformation

This conformation is typical for 1,3-linked β-D-glucopyranose units (Fig. 4.12, b), as occur in the polysaccharide lichenin, found in moss-like plants (lichens):

\[
\text{HO} \quad \text{CH}_2\text{OH} \quad \text{O} \quad \text{O} \quad \text{O}
\]

(4.129)

The formula shows that the helical conformation of the chain is imposed by a U-form geometry of the monomer linkages. Amylose (1,4-linked α-D-glucopyranosyl residues) also has such a geometry, and hence a helical conformation:

\[
\text{HO} \quad \text{CH}_2\text{OH} \quad \text{O} \quad \text{O} \quad \text{O}
\]

(4.130)

The number of monomers per turn ($n$) and the pitch in the axial direction per residue ($h$) is highly variable in a hollow helical conformation. The value of $n$ is between 2 and ±10, whereas $h$ can be near its limit value of 0. The conformation of a β(1 → 3)-glucan, with $n = 5.64$ and $h = 3.16$ Å, is shown in Fig. 4.12, b. The helical conformation can be stabilized in various ways. When the helix diameter is large, inclusion (clathrate) compounds can be formed (Fig. 4.13, a; cf. 4.4.4.14.3). More extended or stretched chains, with smaller helix diameter,
can form double or triple stranded helices (Fig. 4.13, b; cf. 4.4.4.3.2 and 4.4.4.14.3), while strongly-stretched chains, in order to stabilize the conformation, have a zigzag, pleated association and are not stranded (Fig. 4.13, c).

4.4.2.3 Crumpled-Type Conformation

This conformation occurs with, for example, 1,2-linked β-D-glucopyranosyl residues (Fig. 4.12, c). This is due to the wrinkled geometry of the monomer O-bridge linkages:

\[
\text{(4.131)}
\]

Here, the \( n \) value varies from 4 up to \(-2\) and \( h \) is 2–3 Å. The conformation reproduced in Fig. 4.12, c has \( n = 2.62 \) and \( h = 2.79 \) Å. The likelihood of such a disorderly form associating into more orderly conformations is low. Polysaccharides of this conformational type play only a negligible role in nature.

4.4.2.4 Loosely-Jointed Conformation

This is typical for glycans with 1,6-linked β-D-glucopyranosyl units, because they exhibit a particularly great variability in conformation. The great flexibility of this glycan-type conformation is based on the nature of the connecting bridge between the monomers. The bridge has three free rotational bonds and, furthermore, the sugar residues are further apart:

\[
\text{(4.132)}
\]

4.4.2.5 Conformations of Heteroglycans

The examples considered so far have demonstrated that a prediction is possible for a homoglycan conformation based on the geometry of the bonds of the monomer units which maintain the oxygen bridges. It is more difficult to predict the conformation of a heteroglycan with a periodic sequence of several monomers, which implies different types of conformations. Such a case is shown by \( \iota \)-carrageenan, in which the \( \beta \)-D-galactopyranosyl-4-sulfate units have a U-form geometry, while the 3,6-anhydro-\( \alpha \)-D-galactopyranosyl-2-sulfate residues have a zigzag geometry:

\[
\text{(4.133)}
\]

Calculations have shown that conformational possibilities vary from a shortened, compressed ribbon band type to a stretched helix type. X-ray diffraction analyses have proved that a stretched helix exists, but as a double stranded helix in order to stabilize the conformation (cf. 4.4.4.3.2 and Fig. 4.19).

4.4.2.6 Interchain Interactions

It was outlined in the introductory section (cf. 4.4.1) that the periodically arranged monosaccharide sequence in a polysaccharide can be interrupted by nonperiodic segments. Such
sequence interferences result in conformational disorders. This will be explained in more detail with τ-carrageenan, mentioned above, since it will shed light on the gel-setting mechanism of macromolecules in general.

Initially, a periodic sequence of alternating units of β-D-galactopyranose-4-sulfate (I, conformation $^4C_1$) and α-D-galactopyranose-2,6-disulfate (II, conformation $^4C_1$) is built up in carrageenan biosynthesis:

$$\text{(4.134)}$$

When the biosynthesis of the chain is complete, an enzyme-catalyzed reaction eliminates sulfate from most of α-D-galactopyranose-2,6-disulfate (II), transforming the unit to 3,6-anhydro-α-D-galactopyranose-2-sulfate (III, conformation $^1C_4$). This transformation is associated with a change in linkage geometry. Some II-residues remain in the sequence, acting as interference sites. While the undisturbed, ordered segment of one chain can associate with the same segment of another chain, forming a double helix, the nonperiodic or disordered segments can not participate in such associations (Fig. 4.14).

In this way, a gel is formed with a three-dimensional network in which the solvent is immobilized. The gel properties, e.g., its strength, are influenced by the number and distribution of α-D-galactopyranosyl-2,6-disulfate residues, i.e. by a structural property regulated during polysaccharide biosynthesis. The example of the τ-carrageenan gel-building mechanism, involving a chain–chain interaction of sequence segments of orderly conformation, interrupted by randomly-coiled segments corresponding to a disorderly chain sequence, can be applied generally to gels of other macromolecules. Besides a sufficient chain length, the structural prerequisite for gel-setting ability is interruption of a periodic sequence and its orderly conformation. The interruption is achieved by insertion into the chain of a sugar residue of a different linkage geometry (carrageenans, alginates, pectin), by a suitable distribution of free and esterified carboxyl groups (glycuronans) or by insertion of side chains. The interchain associations during gelling (network formation), which involve segments of orderly conformation, can then occur in the form of a double helix (Fig. 4.15,a); a multiple bundle of double helices (Fig. 4.15,b); an association between stretched ribbon-type conformations, such as an egg box model (Fig. 4.15,c); some other similar associations (Fig. 4.15,d); or, lastly, forms consisting of double helix and ribbon-type combinations (Fig. 4.15,e).
4.4.3 Properties

4.4.3.1 General Remarks

Polysaccharides are widely and abundantly distributed in nature, fulfilling roles as:

- Structure-forming skeletal substances (cellulose, hemicellulose and pectin in plants; chitin, mucopolysaccharides in animals).
- Assimilative reserve substances (starch, dextrans, inulin in plants; glycogen in animals).
- Water-binding substances (agar, pectin and alginate in plants; mucopolysaccharides in animals).

As a consequence, polysaccharides occur in many food products and even then they often retain their natural role as skeletal substances (fruits and vegetables) or assimilative nutritive substances (cereals, potatoes, legumes). Isolated polysaccharides are utilized to a great extent in food processing, either in native or modified form, as: thickening or gel-setting agents (starch, alginate, pectin, guaran gum); stabilizers for emulsions and dispersions; film-forming, coating substances to protect sensitive food from undesired change; and inert fillers to increase the proportion of indigestible ballast substances in a diet (cf. 15.2.4.2). Table 4.19 gives an overview of uses in food technology.

The outlined functions of polysaccharides are based on their highly variable properties. They vary from insoluble forms (cellulose) to those with good swelling power and solubility in hot and cold water (starch, guaran gum). The solutions may exhibit low viscosities even at very high concentrations (gum arabic), or may have exceptionally high viscosities even at low concentrations (guaran gum). Some polysaccharides, even at a low concentration, set into a thermoreversible gel (alginites, pectin). While most of the gels melt at elevated temperatures, some cellulose derivatives set into a gel.

These properties and their utilization in food products are described in more detail in section 4.4.4, where individual polysaccharides are covered. Here, only a brief account will be given to relate their properties to their structures in a general way.

4.4.3.2 Perfectly Linear Polysaccharides

Compounds with a single neutral monosaccharide structural unit and with one type of linkage (as occurs in cellulose or amylose) are denoted as perfectly linear polysaccharides. They are usually insoluble in water and can be solubilized only under drastic conditions, e.g. at high temperature, or by cleaving H-bonds with alkalies or other suitable reagents. They readily precipitate from solution (example: starch retrogradation). The reason for these properties is the existence of an optimum structural prerequisite for the formation of an orderly conformation within the chain and also for chain–chain interaction. Often, the conformation is so orderly that a partial crystallinity state develops. Large differences in properties are found within these groups of polysaccharides when there is a change in structural unit, linkage type or molecular weight. This is shown by properties of cellulose, amylose or β-1,3-glucan macromolecules.

4.4.3.3 Branched Polysaccharides

Branched polysaccharides (amylopectin, glycogen) are more soluble in water than their perfectly linear counterparts since the chain–chain interaction is less pronounced and there is a greater extent of solvation of the molecules. Solutions of branched polysaccharides, once dried, are readily rehydrated. Compared to their linear counterparts of equal molecular weights and equal concentrations, solutions of branched polysaccharides have a lower viscosity. It is assumed that the viscosity reflects the “effective volume” of the macromolecule. The “effective volume” is the volume of a sphere with diameter determined by the longest linear extension of the molecule. These volumes are generally larger for linear than for branched molecules (Fig. 4.16). Exceptions are found with highly pleated linear chains. The tendency of branched polysaccharides to precipitate is low. They form a sticky paste at higher concentrations, probably due to side chain–side chain interactions (interpenetration, entanglement). Thus, branched polysaccharides are suitable as binders or adhesives.
Table 4.19. Examples of uses of polysaccharides in foods

<table>
<thead>
<tr>
<th>Area of application/food</th>
<th>Suitable polysaccharides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stabilization of emulsions/suspensions in condensed milk and chocolate milk</td>
<td>Carrageenan, algin, pectin, carboxymethylcellulose</td>
</tr>
<tr>
<td>Stabilization of emulsions in coffee whiteners, low-fat margarines</td>
<td>Carrageenan</td>
</tr>
<tr>
<td>Stabilization of ice cream against ice crystal formation, melting, phase separation;</td>
<td>Algin, carrageenan, agar, gum arabic, gum tragacanth, xanthan gum, guaran gum, locust</td>
</tr>
<tr>
<td>improvement of consistency (smoothness)</td>
<td>bean flour, modified starches, carboxymethylcellulose, methylcellulose</td>
</tr>
<tr>
<td>Water binding, improvement of consistency, yield</td>
<td>Carrageenan, agar, gum tragacanth, karaya gum, guaran gum, locust bean flour, algin,</td>
</tr>
<tr>
<td>increase of soft cheese, cream cheese, cheese preparations</td>
<td>carboxymethylcellulose</td>
</tr>
<tr>
<td>Thicken and gelation of milk in puddings made with and without heating, creams;</td>
<td>Pectin, algin, carrageenan, guaran gum, locust bean flour, carboxymethylcellulose,</td>
</tr>
<tr>
<td>improvement of consistency</td>
<td>modified starches</td>
</tr>
<tr>
<td>Water binding, stabilization of emulsions in meat products (corned beef, sausage)</td>
<td>Agar, karaya gum, guaran gum, locust bean flour</td>
</tr>
<tr>
<td>Jellies for meat, fish, and vegetable products</td>
<td>Algin, carrageenan, agar</td>
</tr>
<tr>
<td>Stabilization and thickening, prevention of synaeresis, freeze-thaw stability of</td>
<td>Gum tragacanth, algin, karaya gum, xanthan gum, guaran gum, locust bean flour,</td>
</tr>
<tr>
<td>soups, sauces, salad dressing, mayonnaise, ketchup; obtaining “body” in low-fat and</td>
<td>carboxymethylcellulose, propylene glycol alginate, modified starches</td>
</tr>
<tr>
<td>low-starch products</td>
<td></td>
</tr>
<tr>
<td>Stabilization of protein foam in beer, whipped cream, meringues, chocolate marshmallows</td>
<td>Algin, carrageenan, agar, gum arabic, karaya gum, xanthan gum</td>
</tr>
<tr>
<td>Prevention of starch retrogradation in bread and cakes, water binding in dough</td>
<td>Agar, guaran gum, locust bean flour, carrageenan, xanthan gum</td>
</tr>
<tr>
<td>Thickening and gelation of fruit pulp (confiture, jams, jellies, fruit pulp for ice</td>
<td>Pectin, algin</td>
</tr>
<tr>
<td>cream and yoghurt)</td>
<td></td>
</tr>
<tr>
<td>Gelation of jelly candies, jelly beans, glaze, icing, water-dessert jellies</td>
<td>Pectin, algin, carrageenan, agar, gum arabic, modified starches</td>
</tr>
<tr>
<td>Sediment stabilization in fruit juices, obtaining “body” in beverage powders</td>
<td>Algin, pectin, propylene glycol alginate, gum arabic, xanthan gum, guaran gum,</td>
</tr>
<tr>
<td>Stabilization of powdery aroma emulsions, encapsulation of aroma substances</td>
<td>methylcellulose, Gum arabic, gum ghatti, xanthan gum</td>
</tr>
</tbody>
</table>

4.4.3.4 Linearly Branched Polysaccharides

Linearly branched polysaccharides, i.e. polymers with a long “backbone” chain and with many short side chains, such as guaran or alkyl cellulose, have properties which are a combination of those of perfectly linear and of branched molecules. The long “backbone” chain is responsible for high solution viscosity. The presence of numerous short side chains greatly weakens interactions between the molecules, as shown by the good solubility and rehydration rates of the molecules and by the stability even of highly concentrated solutions.

4.4.3.5 Polysaccharides with Carboxyl Groups

Polysaccharides with carboxyl groups (pectin, algin, carboxymethyl cellulose) are very soluble as alkali salts in the neutral or alkaline pH range. The molecules are negatively charged due to carboxylate anions and, due to their repulsive charge forces, the molecules are relatively stretched and resist intermolecular associations. The solution viscosity is high and is pH-dependent. Gel setting or precipitation occurs at pH ≤ 3 since electrostatic repulsion ceases to exist. In addition, undissociated carboxyl groups dimerize through
Fig. 4.16. Schematic representation of the “effective volumes” of linear, branched and linearly branched types of polysaccharides

H-bridges. However, a divalent cation is needed to achieve gel setting in a neutral solution.

4.4.3.6 Polysaccharides with Strongly Acidic Groups

Polysaccharides with strongly acidic residues, present as esters along the polymer chains (sulfuric, phosphoric acids, as in furcellaran, carrageenan or modified starch), are also very soluble in water and form highly viscous solutions. Unlike polysaccharides with carboxyl groups, in strongly acidic media these solutions are distinctly stable.

4.4.3.7 Modified Polysaccharides

Modification of polysaccharides, even to a low substitution degree, brings about substantial changes in their properties.

4.4.3.7.1 Derivatization with Neutral Substituents

The solubility in water, viscosity and stability of solutions are all increased by binding neutral substituents to linear polysaccharide chains. Thus the properties shown by methyl, ethyl and hydroxypropyl cellulose correspond to those of guaran and locust bean gum. The effect is explained by interference of the alkyl substituents in chain interactions, which then facilitates hydration of the molecule. An increased degree of substitution increases the hydrophobicity of the molecules and, thereby, increases their solubility in organic solvents.

4.4.3.7.2 Derivatization with Acidic Substituents

Binding acid groups to a polysaccharide (carboxymethyl, sulfate or phosphate groups) also results in increased solubility and viscosity for reasons already outlined. Some derivatized polysaccharides, when moistened, have a pasty consistence.

4.4.4 Individual Polysaccharides

4.4.4.1 Agar

4.4.4.1.1 Occurrence, Isolation

Agar is a gelatinous product isolated from seaweed (red algae class, Rhodophyceae), e.g., Gelidium spp., Pterocladia spp. and Gracilaria spp., by a hot water extraction process. Purification is possible by congealing the gel.

4.4.4.1.2 Structure, Properties

Agar is a heterogenous complex mixture of related polysaccharides having the same backbone chain structure. The main components of the chain are β-D-galactopyranose and 3,6-anhydro-α-L-galactopyranose, which alternate through $1 \rightarrow 4$ and $1 \rightarrow 3$ linkages.
The chains are esterified to a low extent with sulfuric acid. The sulfate content differentiates between the agarose fraction (the main gelling component of agar), in which close to every tenth galactose unit of the chain is esterified, and the agarapectin fraction, which has a higher sulfate esterification degree and, in addition, has pyruvic acid bound in ketal form \([4,6-(l\text{-carboxyethylidene})-D\text{-galactose}].\) The ratio of the two polymers can vary greatly. Uronic acid, when present, does not exceed 1%. Agar is insoluble in cold water, slightly soluble in ethanolamine and soluble in formamide. Agar precipitated by ethanol from a warm aqueous dispersion is, in its moist state, soluble in water at 25 °C, while in the dried state it is soluble only in hot water. Gel setting occurs upon cooling. Agar is a most potent gelling agent as gelation is perceptible even at 0.04%. Gel setting and stability are affected by agar concentration and its average molecular weight. A 1.5% solution sets to a gel at 32–39 °C, but does not melt below 60–97 °C. The great difference between gelling and melting temperatures, due to hysteresis, is a distinct and unique feature of agar.

### 4.4.4.1.3 Utilization

Agar is widely used, for instance in preparing nutritive media in microbiology. Its application in the food industry is based on its main properties: it is essentially indigestible, forms heat resistant gels, and has emulsifying and stabilizing activity. Agar is added to sherbets (frozen desserts of fruit juice, sugar, water or milk) and ice creams (at about 0.1%), often in combination with gum tragacanth or locust (carob) bean gum or gelatin. An amount of 0.1–1% stabilizes yoghurt, some cheeses and candy and bakery products (pastry fillings). Furthermore, agar retards bread staling and provides the desired gel texture in poultry and meat canning. Lastly, agar has a role in vegetarian diets (meat substitute products) and in desserts and pretreated instant cereal products.

### 4.4.4.2 Alginates

#### 4.4.4.2.1 Occurrence, Isolation

Alginates occur in all brown algae (Phaeophyceae) as a skeletal component of their cell walls. The major source of industrial production is the giant kelp, *Macrocystis pyrifera*. Some species of *Laminaria*, *Ascophyllum* and *Sargassum* are also used. Algae are extracted with alkali. The polysaccharide is usually precipitated from the extract by acids or calcium salts.

#### 4.4.4.2.2 Structure, Properties

Alginate building blocks are \(\beta\text{-D-mannuronic}\) and \(\alpha\text{-L-guluronic acids},\) joined by \(1 \rightarrow 4\) linkages:

![Alginate structure](image)

The ratio of the two sugars (mannuronic/guluronic acids) is generally 1.5, with some deviation depending on the source. Alginates extracted from *Laminaria hyperborea* have ratios of 0.4–1.0. Partial hydrolysis of alginate yields chain fragments which consist predominantly of mannuronic or guluronic acid, and also fragments where the two uronic acid residues alternate in a 1:1 ratio. Alginates are linear copolymers consisting of the following structural units:

\[
\begin{align*}
[\rightarrow 4]\cdot\beta\text{-o-ManpA}(1 \rightarrow 4)\cdot\beta\text{-o-ManpA}(1 \rightarrow)\_n \\
[\rightarrow 4]\cdot\alpha\text{-l-GulpA}(1 \rightarrow 4)\cdot\alpha\text{-l-GulpA}(1 \rightarrow)\_m \\
[\rightarrow 4]\cdot\beta\text{-o-ManpA}(1 \rightarrow 4)\cdot\alpha\text{-l-GulpA}(1 \rightarrow)\_n
\end{align*}
\]

The molecular weights of alginates are 32–200 kdal. This corresponds to a degree of polymerization of 180–930. The carboxyl group \(pK\)-values are 3.4–4.4. Alginates are water soluble in the form of alkali, magnesium, ammonia or amine salts. The viscosity of alginate solutions is influenced by molecular weight and the counter ion of the salt. In the absence of di- and trivalent cations or in the presence of a chelating agent, the viscosity is low (“long flow” property). However, with a rise in multivalent cation levels (e.g., calcium) there is a parallel rise in viscosity (“short flow”). Thus, the viscosity can...
be adjusted as desired. Freezing and thawing of a Na-alginate solution containing Ca\(^{2+}\) ions can result in a further rise in viscosity. The curves in Fig. 4.17 show the effect on viscosity of the concentrations of three alginate preparations: low, moderate and high viscosity types. These data reveal that a 1\% solution, depending on the type of alginate, can have a viscosity range of 20–2000 cps. The viscosity is unaffected in a pH range of 4.5–10. It rises at a pH below 4.5, reaching a maximum at pH 3–3.5.

Gels, fibers or films are formed by adding Ca\(^{2+}\) or acids to Na-alginate solutions. A slow reaction is needed for uniform gel formation. It is achieved by a mixture of Na-alginate, calcium phosphate and glucono-δ-lactone, or by a mixture of Na-alginate and calcium sulfate.

Depending on the concentration of calcium ions, the gels are either thermoreversible (low concentration) or not (high concentration). Figure 4.18 shows a schematic section of a calcium alginate gel.

4.4.4.2.3 Derivatives

Propylene glycol alginate is a derivative of economic importance. This ester is obtained by the reaction of propylene oxide with partially neutralized alginic acid. It is soluble down to pH 2 and, in the presence of Ca\(^{2+}\) ions, forms soft, elastic, less brittle and syneresisfree gels.

4.4.4.2.4 Utilization

Alginate is a powerful thickening, stabilizing and gel-forming agent. At a level of 0.25–0.5\% it improves and stabilizes the consistency of fillings for baked products (cakes, pies), salad dressings and milk chocolates, and prevents formation of larger ice crystals in ice creams during storage. Furthermore, alginates are used in a variety of gel products (cold instant puddings, fruit gels, dessert gels, onion rings, imitation caviar) and are applied to stabilize fresh fruit juice and beer foam.

4.4.4.3 Carrageenans

4.4.4.3.1 Occurrence, Isolation

Red sea weeds (Rhodophyceae) produce two types of galactans: agar and agar-like polysaccharides, composed of D-galactose and 3,6-anhydro-L-galactose residues, and carrageenans and related polysaccharides, composed of D-galactose and 3,6-anhydro-D-galactose which are partially sulfated as 2-, 4- and 6-sulfates and 2,6-disulfates. Galactose residues are alternatively linked by 1 → 3 and 1 → 4 linkages. Carrageenans are isolated from Chondrus (Chondrus crispus, the Irish moss), Eucheuma, Gigartina, Gloiopeltis and Iridaea species by hot
water extraction under mild alkaline conditions, followed by drying or isolate precipitation.

4.4.4.3.2 Structure, Properties

Carrageenans are a complex mixture of various polysaccharides. They can be separated by fractional precipitation with potassium ions. Table 4.20 compiles data on these fractions and their monosaccharide constituents. Two major fractions are \( \kappa \) (gelling and K\(^+\)-insoluble fraction) and \( \lambda \) (nongelling, K\(^+\)-soluble).

Table 4.20. Building blocks of carrageenans

<table>
<thead>
<tr>
<th>Carrageenan</th>
<th>Monosaccharide building block</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \kappa )-Carrageenan</td>
<td>D-Galactose-4-sulfate, 3,6-anhydro-D-galactose-2-sulfate</td>
</tr>
<tr>
<td>( \xi )-Carrageenan</td>
<td>D-Galactose-4-sulfate, 3,6-anhydro-D-galactose</td>
</tr>
<tr>
<td>( \lambda )-Carrageenan</td>
<td>D-Galactose-2-sulfate, D-galactose-2,6-disulfate</td>
</tr>
<tr>
<td>( \mu )-Carrageenan</td>
<td>D-Galactose-4-sulfate, D-galactose-6-sulfate, 3,6-anhydro-D-galactose</td>
</tr>
<tr>
<td>( \nu )-Carrageenan</td>
<td>D-Galactose-4-sulfate, D-galactose-2,6-disulfate, 3,6-anhydro-D-galactose</td>
</tr>
<tr>
<td>Furcellaran</td>
<td>D-Galactose-D-galactose-2-sulfate, D-galactose-4-sulfate, D-galactose-6-sulfate, 3,6-anhydro-D-galactose</td>
</tr>
</tbody>
</table>

\( \kappa \)-Carrageenan is composed of D-galactose, 3,6-anhydro-D-galactose and ester-bound sulfate in a molar ratio of 6:5:7. The galactose residues are essentially fully sulfated in position 4, whereas the anhydrogalactose residues can be sulfated in position 2 or substituted by \( \alpha \)-D-galactose-6-sulfate or -2,6-disulfate. A typical sequence of \( \kappa \) (or \( \iota \))-carrageenan is:

The sequence favors the formation of a double-stranded helix (Fig. 4.19). \( \lambda \)-Carrageenan contains as the basic building block \( \beta \)-D-Galp\((1 \rightarrow 4)\)-\( \alpha \)-D-Galp (cf. Formula 4.139), which is joined through a 1,3-glycosidic linkage to the polymer. Position 6 of the second galactose residue is esterified with sulfuric acid as is ca. 70% of position 2 of both residues. The high sulfate content favors the formation of a zigzag ribbon-shaped conformation.

The molecular weights of \( \kappa \) - and \( \lambda \)-carrageenans are 200–800 kdal. The water solubility increases

Fig. 4.19. \( \iota \)-Carrageenan conformation. a Double helix, b single coil is presented to clarify the conformation (according to Rees, 1977)
as the carrageenan sulfate content increases and as the content of anhydrosugar residue decreases. The viscosity of the solution depends on the carrageenan type, molecular weight, temperature, ions present and carrageenan concentration. As observed in all linear macromolecules with charges along the chain, the viscosity increases exponentially with the concentration (Fig. 4.20). Aqueous \( \kappa \)-carrageenan solutions, in the presence of ammonium, potassium, rubidium or caesium ions, form thermally reversibly gels. This does not occur with lithium and sodium ions. This strongly suggests that gel-setting ability is highly dependent on the radius of the hydrated counter ion. The latter is about 0.23 nm for the former group of cations, while hydrated lithium (0.34 nm) and sodium ions (0.28 nm) exceed the limit. The action of cations is visualized as a zipper arrangement between aligned segments of linear polymer sulfates, with low ionic radius cations locked between alternating sulfate residues. Gel-setting ability is probably also due to a mechanism based on formation of partial double helix structures between various chains. The extent of intermolecular double helix formation, and thus the gel strength, is greater, the more uniform the chain sequences are. Each substitution of a 3,6-anhydrogalactose residue by another residue, e.g., galactose-6-sulfate, results in a kink within the helix and, thereby, a decrease in gelling strength. The helical conformation is also affected by the position of sulfate groups. The effect is more pronounced with sulfate in the 6-position, than in 2- or 4-positions. Hence, the gel strength of \( \kappa \)-carrageenan is dependent primarily on the content of esterified sulfate groups in the 6-position. The addition of carubin, which is itself non-gelling, to \( \kappa \)-carrageenan produces more rigid, more elastic gels that have a lower tendency towards synaeresis. Carubin apparently prevents the aggregation of \( \kappa \)-carrageenan helices. The 6-sulfate group can be removed by heating carrageenans with alkali, yielding 3,6-anhydrogalactose residues. This elimination results in a significantly increased gel strength. Carrageenans and other acidic polysaccharides coagulate proteins when the pH of the solution is lower than the proteins’ isoelectric points. This can be utilized for separating protein mixtures.

4.4.4.3.3 Utilization

Carrageenan utilization in food processing is based on the ability of the polymer to gel, to increase solution viscosity and to stabilize emulsions and various dispersions. A level as low as 0.03% in chocolate milk prevents fat droplet separation and stabilizes the suspension of cocoa particles. Carrageenans prevent syneresis in fresh cheese and improve dough properties and enable a higher amount of milk powder incorporation in baking. The gelling property in the presence of K\(^+\) salt is utilized in desserts and canned meat. Protein fiber texture is also improved. Protein sedimentation in condensed milk is prevented by carrageenans which, like \( \kappa \)-casein, prevent milk protein coagulation by calcium ions. Carrageenans are also used to stabilize ice cream and clarify beverages.

4.4.4.4 Furcellaran

4.4.4.4.1 Occurrence, Isolation

Furcellaran (Danish agar) is produced from red sea weed (algae *Furcellaria fastigiata*). Production began in 1943 when Europe was cut off from its agar suppliers. After alkali pretreatment of algae, the polysaccharide is isolated using hot water. The extract is then concentrated under vacuum and seeded with 1–1.5% KCl solution. The
separated gel threads are concentrated further by freezing, the excess water is removed by centrifugation or pressing and, lastly, the polysaccharide is dried. The product is a K-salt and contains, in addition, 8–15% occluded KCl.

4.4.4.4.2 Structure, Properties

Furcellaran is composed of D-galactose (46–53%), 3,6-anhydro-D-galactose (30–33%) and sulfated portions of both sugars (16–20%). The structure of furcellaran is similar to Χ-carrageenan. The essential difference is that Χ-carrageenan has one sulfate ester per two sugar residues, while furcellaran has one sulfate ester residue per three to four sugar residues. Sugar sulfates identified are: D-galactose-2-sulfate, -4-sulfate and -6-sulfate, and 3,6-anhydro-D-galactose-2-sulfate. Branching of the polysaccharide chain can not be excluded. Furcellaran forms thermally reversible aqueous gels by a mechanism involving double helix formation, similar to Χ-carrageenan.

The gelling ability is affected by the polysaccharide polymerization degree, amount of 3,6-anhydro-D-galactose, and by the radius of the cations present. K\(^+\), NH\(^+_4\), Rb\(^+\) and Cs\(^+\) from very stable, strong gels. Ca\(^{2+}\) has a lower effect, while Na\(^+\) prevents gel setting. Addition of sugar affects the gel texture, which goes from a brittle to a more elastic texture.

4.4.4.4.3 Utilization

Furcellaran, with milk, provides good gels and therefore it is used as an additive in puddings. It is also suitable for cake fillings and icings. In the presence of sucrose, it gels rapidly and retains good stability, even against food grade acids. Furcellaran has the advantage over pectin in marmalades since it allows stable gel setting at a sugar concentration even below 50–60%. The required amount of polysaccharide is 0.2–0.5%, depending on the marmalade’s sugar content and the desired gel strength. To keep the hydrolysis extent low, a cold aqueous 2–3% solution of furcellaran is mixed into a hot, cooked slurry of fruits and sugar.

Furcellaran is also utilized in processed meat products, such as spreadable meat pastes and pastry fillings. It facilitates protein precipitation during brewing of beer and thus improves the final clarification of the beer.

4.4.4.5 Gum Arabic

4.4.4.5.1 Occurrence, Isolation

Gum arabic is a tree exudate of various Acacia species, primarily Acacia Senegal, and is obtained as a result of tree bark injury. It is collected as air-dried droplets with diameters from 2–7 cm. The annual yield per tree averages 0.9–2.0 kg. The major producer is Sudan, with 50–60,000 t/annum, followed by several other African countries. Gum arabic has been known since ancient Egypt as “kami”, an adhesive for pigmented paints.

4.4.4.5.2 Structure, Properties

Gum arabic is a mixture of closely related polysaccharides, with an average molecular weight range of 260–1160 kdal. The main structural units, with molar proportions for the gum exudate A. senegal given in brackets, are L-arabinose (3.5), L-rhamnose (1.1), D-galactose (2.9) and D-glucuronic acid (1.6). The proportion varies significantly depending on the Acacia species. Gum arabic has a major core chain built of β-D-galactopyranosyl residues linked by 1 → 3 bonds, in part carrying side chains attached at position 6 (cf. Formula 4.140).

Gum arabic occurs neutral or as a weakly acidic salt. Counter ions are Ca\(^{2+}\), Mg\(^{2+}\) and K\(^+\). Solubilization in 0.1 mol/l HCl and subsequent precipitation with ethanol yields the free acid. Gum arabic exhibits marked emulsifying and film-forming properties, which are caused not only by its structure, but also by the slight admixture (ca. 2%) of a protein. The serine and threonine residues of this protein are thought to be covalently bound to the carbohydrate.

The interfacial activity of gum arabic is low compared to that of proteins. The proportion of gum arabic to oil used in formulations has to be ap-
approximately 1:1. In contrast, a protein oil ratio of about 1:10 is used in an emulsion stabilized by milk proteins.

Gum arabic is very soluble in water and solutions of up to 50% gum can be prepared. The solution viscosity starts to rise steeply only at high concentrations (Fig. 4.21). This property is unlike that of many other polysaccharides, which provide highly viscous solutions even at low concentrations (Table 4.21).

**Table 4.21. Viscosity (mPas) of polysaccharides in aqueous solution as affected by concentration (25 °C)**

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Gum arabic</th>
<th>Tragacanth</th>
<th>Carrageenan</th>
<th>Sodium alginate</th>
<th>Methyl cellulose</th>
<th>Locust bean gum</th>
<th>Guaran gum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>54</td>
<td>57</td>
<td>214</td>
<td>39</td>
<td>59</td>
<td>3025</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>906</td>
<td>397</td>
<td>3760</td>
<td>512</td>
<td>1114</td>
<td>25,060</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>10,605</td>
<td>4411</td>
<td>29,400</td>
<td>3850</td>
<td>8260</td>
<td>111,150</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>44,275</td>
<td>25,356</td>
<td>12,750</td>
<td>39,660</td>
<td>302,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>111,000</td>
<td>51,425</td>
<td>67,575</td>
<td>121,000</td>
<td>510,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>183,500</td>
<td>4163</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>41</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>936</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>4163</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.4.4.5.3 Utilization

Gum arabic is used as an emulsifier and stabilizer, e.g., in baked products. It retards sugar crystallization and fat separation in confectionery products and large ice crystal formation in ice creams, and can be used as a foam stabilizer in beverages. Gum arabic is also applied as a flavor fixative in the production of encapsulated, powdered aroma concentrates. For example, essential oils are emulsified with gum arabic solution and then spray-dried. In this process, the polysaccharide forms a film surrounding the oil droplet, which then protects the oil against oxidation and other changes.

4.4.4.6 Gum Ghatti

4.4.4.6.1 Occurrence

Gum ghatti is an exudate from the tree *Anogeissus latifolia* found in India and Ceylon.

4.4.4.6.2 Structure, Properties

The building blocks are L-arabinose, D-galactose, D-mannose, D-xylose, and D-glucuronic acid. L-Rhamnose has also been detected. The sugars are partially acetylated (5.5% acetyl groups based on dry weight). Three characteristic structural elements have been detected (cf. Formula 4.141). This acidic polysaccharide occurs as a Ca/Mg salt. Gum ghatti is soluble in water to the extent of ca. 90% and dispersible. Although it produces solutions that are more viscous than gum arabic, it is less soluble.

4.4.4.6.3 Utilization

Like gum arabic, gum ghatti can be used for the stabilization of suspensions and emulsions.

4 Carbohydrates

\[
\begin{align*}
\text{---} & \rightarrow 4)-\beta-\text{Glc}pA-(1 \rightarrow 6)-\beta-\text{Gal}p-(1 \rightarrow \cdots) & R = \text{\_\_Ara} \\
& -\beta-\text{Rha} \\
& \downarrow \\
3 & \downarrow & [\text{\_\_Ara}],_\text{\_\_Ara} \\
R & 6 & 6 \\
\text{---} & \rightarrow 3)-\beta-\text{Glc}pA-(1 \rightarrow 2)-\beta-\text{Man}p-(1 \rightarrow 2)-\beta-\text{Man}p-(1 \rightarrow \cdots) \\
& \uparrow \\
& R \\
& \downarrow \\
3 & \downarrow & 4 \\
\text{---} & \rightarrow 3)-\beta-\text{Gal}p-(1 \rightarrow 6)-\beta-\text{Gal}p-(1 \rightarrow 6)-\beta-\text{Gal}p-(1 \rightarrow 3)-\text{\_\_Arap}-(1 \rightarrow \cdots) \\
& \uparrow \\
& 3 \\
R & R
\end{align*}
\]

(4.141)
4.4.4.7 Gum Tragacanth

4.4.4.7.1 Occurrence

Gum tragacanth is a plant exudate collected from *Astragalus* species shrubs grown in the Middle East (Iran, Syria, Turkey).

4.4.4.7.2 Structure, Properties

Gum tragacanth consists of a water-soluble fraction, the so-called tragacanthic acid, and the insoluble swelling component, bassorin. Tragacanthic acid contains 43% of D-galacturonic acid, 40% of D-xylose, 10% of L-fucose, and 4% of D-galactose. Like pectin, it is composed of a main polygalacturonic acid chain which bears side chains made of the remaining sugar residues (Formula 4.142). Bassorin consists of 75% of L-arabinose, 12% of D-galactose, 3% of D-galacturonic acid methyl ester, and L-rhamnose. Its molecular weight is about 840 kdal. The molecules are highly elongated (450 × 1.9 nm) in aqueous solution and are responsible for the high viscosity of the solution (Table 4.21). As shown in Fig. 4.22, the viscosity is highly dependent on shear rate.

4.4.4.7.3 Utilization

Gum tragacanth is used as a thickening agent and a stabilizer in salad dressings (0.4–1.2%) and in fillings and icings in baked goods. As an additive in ice creams (0.5%), it provides a soft texture.

4.4.4.8 Karaya Gum

4.4.4.8.1 Occurrence

Karaya gum, also called Indian tragacanth, is an exudate from an Indian tree of the *Sterculia ureus* and other *Sterculia* species.

4.4.4.8.2 Structure, Properties

The building blocks are D-galactose, L-rhamnose, D-galacturonic acid, and L-glucuronic acid. The sugars are partially acetylated (13% acetyl groups based on dry weight). The molecule consists of three main chains which are polymers of different disaccharide units (cf. Formula 4.143). The main chains carry side chains and are also covalently linked via the side chains.

\[
\cdots \to 4)-\alpha-\d-galpA-(1 \to 4)-\alpha-\d-galpA-(1 \to 4)-\alpha-\d-galpA-(1 \to 4)-\alpha-\d-galpA\ldots
\]

\[
\begin{array}{llll}
3 & 3 & 3 \\
1 & 1 & 1 \\
\beta-\d-xylp & \beta-\d-xylp & \beta-\d-xylp \\
2 & 2 & 1 \\
1 & 1 & 1 \\
\alpha-\l-fucp & \beta-\d-galp & \\
\end{array}
\] (4.142)
As a result of the strong cross-linkage, this polysaccharide is insoluble in water and resistant to enzymes and microorganisms. However, it swells greatly even in cold water. Suspensions have a pasty consistency at concentrations of more than 3%.

4.4.4.8.3 Utilization

Karaya gum is used as a water binder (soft cheese), a binding agent (meat products like corned beef, sausages), a stabilizer of protein foams (beer, whipped cream, meringues), and as a thickener (soups, sauces, salad dressings, mayonnaise, ketchup). It increases the freeze-thaw stability of products, prevents syneresis of gels, and provides “body”.

4.4.4.9 Guaran Gum

4.4.4.9.1 Occurrence, Isolation

Guar flour is obtained from the seed endosperm of the leguminous plant *Cyamopsis tetragonoloba*. The seed is decoated and the germ removed. In addition to the polysaccharide guaran, guar flour contains 10–15% moisture, 5–6% protein, 2.5% crude fiber and 0.5–0.8 ash. The plant is cultivated for forage in India, Pakistan and the United States (Texas).

4.4.4.9.2 Structure, Properties

Guaran gum consists of a chain of β-D-mannopyranosyl units joined by 1 → 4 linkages. Every second residue has a side chain, a D-galactopyranosyl residue that is bound to the main chain by an α(1 → 6) linkage (cf. Formula 4.126). Guaran gum forms highly viscous solutions (Table 4.21), the viscosity of which is shear rate dependent (Fig. 4.23).
4.4.4.10.2 Structure, Properties

The main locust bean polysaccharide is similar to that of guar gum: a linear chain of $1 \rightarrow 4$ linked $\beta$-D-mannopyranosyl units, with $\alpha$-D-galactopyranosyl residues $1 \rightarrow 6$ joined as side chains. The ratio mannose/galactose is 3 to 6; this indicates that, instead of every second mannose residue, as in guar gum, only every 4th to 5th is substituted at the C-6 position with a galactose molecule.

The molecular weight of the galactomannan is close to 310 kdal. Physical properties correspond to those of guar gum, except the viscosity of the solution is not as high (cf. Table 4.21).

4.4.4.10.3 Utilization

Locust bean flour is used as a thickener, binder and stabilizer in meat canning, salad dressings, sausages, soft cheeses and ice creams. It also improves the water binding capacity of dough, especially when flour of low gluten content is used.

4.4.4.11 Tamarind Flour

4.4.4.11.1 Occurrence, Isolation

Tamarind is one of the most important and widely grown trees of India (*Tamarindus indica*; date of India). Its brown pods contain seeds which are rich in a polysaccharide that is readily extracted with hot water and, after drying, recovered in a powdered form.

4.4.4.11.2 Structure, Properties

The polysaccharide consists of D-galactose (1), D-xylose (2) and D-glucose (3), with respective molar ratios given in brackets. L-Arabinose is also present. The suggested structure is presented in Formula 4.145.

The polysaccharide forms a stable gel over a wide pH range. Less sugar is needed to achieve a desired gel strength than in corresponding pectin gels (Fig. 4.24). The gels exhibit only a low syneresis phenomenon.
4.4.4.11.3 Utilization

The tamarind seed polysaccharide is a suitable substitute for pectin in the production of marmalades and jellies. It can be used as a thickening agent and stabilizer in ice cream and mayonnaise production.

### 4.4.4.12 Arabinogalactan from Larch

#### 4.4.4.12.1 Occurrence, Isolation

Coniferous larch-related woods (Larix species; similar to pine, but shed their needle-like leaves) contain a water-soluble arabinogalactan of 5–35% of the dry weight of the wood. It can be isolated from chipped wood by a counter-current extraction process, using water or dilute acids. The extract is then usually drum dried.

#### 4.4.4.12.2 Structure, Properties

The polysaccharide consists of straight chain \( \beta-D \)-galactopyranosyl units joined by \( 1 \rightarrow 3 \) linkages and, in part, has side chains of galactose and arabinose residues bound to positions 4 and 6. The suggested structure is given in Formula 4.146.

In general, the polysaccharide is highly branched. The molecular weight is 50–70 kdal. The molecule is nearly spherical in shape, so its aqueous solution behaves like a Newtonian fluid. The viscosity is exceptionally low. At a temperature of 20°C, the viscosity of a 10% solution is 1.74 cps, a 30% solution 7.8 cps at pH 4 or 8.15 cps at pH 11, and a 40% solution 23.5 cps. These data show that the viscosity is practically unaffected by pH. The solution acquires a thick paste consistency only at concentrations exceeding 60%.

#### 4.4.4.12.3 Utilization

Arabinogalactan, due to its good solubility and low viscosity, is used as an emulsifier and stabilizer, and as a carrier substance in essential oils, aroma formulations, and sweeteners.

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**Fig. 4.24.** Gel strength of (a) tamarind flour and (b) pectin from lemons versus saccharose concentration (according to Whistler, 1973)
4.4.4.13 Pectin

4.4.4.13.1 Occurrence, Isolation

Pectin is widely distributed in plants. It is produced commercially from peels of citrus fruits and from apple pomace (crushed and pressed residue). It is 20–40% of the dry matter content in citrus fruit peel and 10–20% in apple pomace. Extraction is achieved at pH 1.5–3 at 60–100 °C. The process is carefully controlled to avoid hydrolysis of glycosidic and ester linkages. The extract is concentrated to a liquid pectin product or is dried by spray- or drum-drying into a powdered product. Purified preparations are obtained by precipitation of pectin with ions which form insoluble pectin salts (e.g. Al$^{3+}$), followed by washing with acidified alcohol to remove the added ions, or by alcoholic precipitation using isopropanol and ethanol.

4.4.4.13.2 Structure, Properties

Pectin is a polysaccharide mixture with a complicated structure containing at least 65% of galacturonic acid (GalA). Three structural elements are involved in the make-up of a pectin molecule: a homogalacturonan (cf. Formula 4.147) consisting of (1 → 4) linked α-D-GalA, a galacturonan with differently arranged side chains (building blocks: apirose, fucose, arabinose, xylose), and a rhamnogalacturonan with a backbone consisting of the disaccharide units [(1 → 4)-α-D-GalA-(1 → 2)-α-L-Rha-(1 →)] and with its rhamnose residues linked by arabinan and galactan chains. In pectins, the GalA residues

\[ \text{R: COO}^\circ, \text{COOCH}_3 \]  

(4.147)

are esterified to a variable extent with methanol, while the HO-groups in 2- and 3-positions may be acetylated to a small extent. Pectin stability is highest at pH 3–4. The glycosidic linkage hydrolyzes in a stronger acidic medium. In an alkaline medium, both linkages, ester and glycosidic, are split to the same extent, the latter by an elimination reaction (cf. Formula 4.148). The elimination reaction occurs more readily with galacturonic acid units having an esterified carboxyl group, since the H-atom on C-5 is more acidic than with residues having free carboxyl groups.

At a pH of about 3, and in the presence of Ca$^{2+}$ ions also at higher pH’s, pectin forms a thermally reversible gel. The gel-forming ability, under comparable conditions, is directly proportional to the molecular weight and inversely proportional to the esterification degree. For gel formation, low-ester pectins require very low pH values and/or calcium ions, but they gelatinize in the presence of a relatively low sugar content. High-ester pectins require an increasing amount of sugar with rising esterification degree. The gelsetting time for high ester pectins is longer than that for pectin products of low esterification degree (Table 4.22). Apart from the degree of esterification, gel formation is also influenced by the distribution of the ester groups in the pectin molecule.

\[ \text{HO-} + \text{H}^\circ \]  

(4.148)
Table 4.22. Gelling time of pectins with differing degrees of esterification

<table>
<thead>
<tr>
<th>Pectin type</th>
<th>Esterification degree (%)</th>
<th>Gelling timea (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast gelling</td>
<td>72–75</td>
<td>20–70</td>
</tr>
<tr>
<td>Normal</td>
<td>68–71</td>
<td>100–135</td>
</tr>
<tr>
<td>Slow gelling</td>
<td>62–66</td>
<td>180–250</td>
</tr>
</tbody>
</table>

a Difference between the time when all the prerequisites for gelling are fulfilled and the time of actual gel setting.

4.4.4.13.3 Utilization

Since pectin can set into a gel, it is widely used in marmalade and jelly production. Standard conditions to form a stable gel are, for instance: pectin content <1%, sucrose 58–75% and pH 2.8–3.5. In low-sugar products, low-ester pectin is used in the presence of Ca$^{2+}$ ions. Pectin is also used to stabilize soured milk beverages, yoghurts and ice creams.

4.4.4.14 Starch

4.4.4.14.1 Occurrence, Isolation

Starch is widely distributed in various plant organs as a storage carbohydrate. As an ingredient of many foods, it is also the most important carbohydrate source in human nutrition. In addition, starch and its derivatives are important industrially, for example, in the paper and textile industries.

Starch is isolated mainly from the sources listed in Table 4.23. Starch obtained from corn, potatoes, cassava, and wheat in the native and modified form accounted for 99% of the world production in 1980. Some other starches are also available commercially. Recently, starches obtained from legumes (peas, lentils) have become more interesting because they have properties which appear to make them a suitable substitute for chemically modified starches in a series of products.

Starches of various origin have individual, characteristic properties which go back to the shape, size, size distribution, composition, and crystallinity of the granules. The existing connections are not yet completely understood on a molecular basis.

Table 4.23. Raw materials for starch

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Starch production 1980a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw materials of industrial importance</td>
<td></td>
</tr>
<tr>
<td>Corn</td>
<td>77</td>
</tr>
<tr>
<td>Waxy corn</td>
<td></td>
</tr>
<tr>
<td>Potato</td>
<td>10</td>
</tr>
<tr>
<td>Cassava</td>
<td>8</td>
</tr>
<tr>
<td>Wheat</td>
<td>4</td>
</tr>
<tr>
<td>Rice</td>
<td></td>
</tr>
<tr>
<td>Waxy rice</td>
<td></td>
</tr>
<tr>
<td>Other raw materials</td>
<td></td>
</tr>
<tr>
<td>Sago palm</td>
<td>Kouzu</td>
</tr>
<tr>
<td>Sweet potato</td>
<td>Water chestnut</td>
</tr>
<tr>
<td>Arrowroot</td>
<td>Edible canna</td>
</tr>
<tr>
<td>Negro corn</td>
<td>Mungo bean</td>
</tr>
<tr>
<td>Lotus root</td>
<td></td>
</tr>
<tr>
<td>Taro</td>
<td>Lentil</td>
</tr>
</tbody>
</table>

a % of the world production.

In some cases, e.g., potato tubers, starch granules occur free, deposited in cell vacuoles; hence, their isolation is relatively simple. The plant material is disintegrated, the starch granules are washed out with water, and then sedimented from the “starch milk” suspension and dried. In other cases, such as cereals, the starch is embedded in the endosperm protein matrix, hence granule isolation is a more demanding process. Thus, a counter-current process with water at 50°C for 36–48 h is required to soften corn (steeping step of processing). The steeping water contains 0.2% SO$_2$ in order to loosen the protein matrix and, thereby, to accelerate the granule release and increase the starch yield. The corn grain is then disintegrated. The germ, due to its high oil content, has a low density and is readily separated by flotation. It is the source for corn oil isolation (cf. 14.3.2.2.4). The protein and starch are then
Carbohydrates separated in hydrocyclones. The separation is based on density difference (protein < starch). The protein by-product is marketed as animal feed or used for production of a protein hydrolysate (seasoning). The recovered starch is washed and dried.

In the case of wheat flour, a dough is made first, from which a raw starch suspension is washed out. After separation of fiber particles from this suspension, the starch is fractionated by centrifugation. In addition to the relatively pure primary starch, a finer grained secondary starch is obtained which contains pentosans. The starch is then dried and further classified. The residue, gluten (cf. 15.1.5), serves, e.g., as a raw material in the production of food seasoning (cf. 12.7.3.5) and in the isolation of glutamic acid. If dried gently, it retains its baking quality and is used as a flour improver. In the case of rye, the isolation of starch is impeded by the relatively high content of swelling agents. Starch isolated from the tubers of various plants in tropical countries is available on the market under a variety of names (e.g., canna, maranta, and tacca starch). The real sago is the product obtained from the pith of the sago palm.

Starch is a mixture of two glucans, amylose and amylopectin (cf. 4.4.4.14.3 and 4.4.4.14.4). Most starches contain 20–30% amylose (Table 4.24). New corn cultivars (amylomaize) have been developed which contain 50–80% amylose. The amylose can be isolated from starch, e.g., by crystallization of a starch dispersion, usually in the presence of salts (MgSO₄) or by precipitation with a polar organic compound (alcohols, such as n-butanol, or lower fatty acids, such as caprylic or capric), which forms a complex with amylose and thus enhances its precipitation.

Normal starch granules contain 70–80% amylopectin, while some corn cultivars and millet, denoted as waxy maize or waxy millet, contain almost 100% amylopectin.

4.4.4.14.2 Structure and Properties of Starch Granules

Starch granules are formed in the amyloplasts. These granules are simple or compound and consist of concentric or eccentric layers of varying density. They are of varying size (2–150 μm), size distribution, and shape (Table 4.24). In addition to amylose and amylopectin, they usually contain small amounts of proteins and lipids. They are examined by using various physical methods, including light microscopy, small-angle light scattering, electron microscopy, X-ray diffraction, small-angle neutron scattering, and small-angle X-ray scattering. On the basis of X-ray diffraction experiments, starch granules are said to have a semicrystalline character, which indicates a high degree of orientation of the glucan molecules. About 70% of the mass of a starch granule is regarded as amorphous and ca. 30% as crystalline (Table 4.24). The amorphous regions contain the main amount of amylose, but also a considerable part of the amylopectin. The crystalline regions consist primarily of amylopectin. Although this finding was surprising at first because of the branched structure of amylopectin (cf. 4.4.4.14.4), it was deduced from the fact that amylose can be dissolved out of the granule without disturbing the crystalline character and that even amylose-free starches, like waxy corn starch, are semicrystalline. The degree of crystallinity depends on the water content. It is 24% for air-dried potato starch (19.8% of water), 29–35% for the wetted product (45–55% of water), and only 17% for starch dried via P₂O₅ and subsequently rehydrated. On the basis of results obtained from different physical methods, the model shown in Fig. 4.25 is under discussion for the crystalline regions of the starch granule. It contains double helices of amylopectin (cf. 4.4.4.14.4), mixed amylose/amylopectin double helices, V helices of amylose with enclosed lipid (cf. 4.4.4.14.3), free amylose, and free lipid.

With the aid of X-ray diffraction diagrams, native starches can be divided into types A, B, and C. An additional form, called the V-type, occurs in swollen granules (Fig. 4.26). While types A and B are real crystalline modifications, the C-type is a mixed form. The A-type is largely present in cereal starches, and the B-type in potatoes, amylomaize, and in retrograded starches (resistant starch, cf. 4.4.4.16.3). The C-type is not only observed in mixtures of corn and potato starches, but it is also found in various legume starches. When suspended in cold water, air-dried starch granules swell with an increase in diameter of 30–40%. If this suspension is heated, irreversible
### Table 4.24. Shape, composition, and properties of different starch granules

<table>
<thead>
<tr>
<th>Source</th>
<th>Shape&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Diameter (µm)</th>
<th>Crystallinity (%)</th>
<th>Gelatinization temperature (°C)</th>
<th>Swelling at 95°C&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Amylose Percentage (%)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Amylopectin Polymerisation degree</th>
<th>Iodine binding constant&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Amylopectin Polymerisation degree&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cereal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wheat</td>
<td>lp</td>
<td>2–38</td>
<td>36</td>
<td>53–65</td>
<td>21</td>
<td>22–28</td>
<td>2100</td>
<td>0.21</td>
<td>19–20</td>
</tr>
<tr>
<td>Rye</td>
<td>l</td>
<td>12–40</td>
<td></td>
<td>57–70</td>
<td>28</td>
<td>22–29</td>
<td>1850</td>
<td>0.74</td>
<td>26</td>
</tr>
<tr>
<td>Barley</td>
<td>l</td>
<td>2–5</td>
<td></td>
<td>56–62</td>
<td>24</td>
<td>28</td>
<td>940</td>
<td>0.91</td>
<td>25–26</td>
</tr>
<tr>
<td>Corn</td>
<td>p</td>
<td>5–25</td>
<td></td>
<td>62–70</td>
<td>64</td>
<td>0–1</td>
<td>1300</td>
<td>0.11</td>
<td>23</td>
</tr>
<tr>
<td>Amylomaize</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Waxy corn</td>
<td>p</td>
<td>39</td>
<td></td>
<td>63–72</td>
<td>64</td>
<td>0–1</td>
<td>1300</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>Oats</td>
<td></td>
<td>5–15</td>
<td></td>
<td>56–62</td>
<td>27</td>
<td>1300</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice</td>
<td>p</td>
<td>3–8</td>
<td>38</td>
<td>61–78</td>
<td>19</td>
<td>14–32</td>
<td></td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>Waxy rice</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Millet</td>
<td>p,s</td>
<td>4–12</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Sorghum</td>
<td>p,s</td>
<td>4–24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waxy sorghum</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>Legumes</strong></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Horsebean</td>
<td>s,o</td>
<td>17–31</td>
<td></td>
<td>64–67</td>
<td>32–34</td>
<td>1800</td>
<td>1.03</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Smooth pea</td>
<td>n(si)</td>
<td>5–10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wrinkled pea</td>
<td>n(c)</td>
<td>30–40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Roots and tubers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potato</td>
<td>e</td>
<td>15–100</td>
<td>25</td>
<td>58–66</td>
<td>23</td>
<td>3200</td>
<td>0.58</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Cassava</td>
<td>semi-s,s</td>
<td>5–35</td>
<td>38&lt;sup&gt;f&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> l = lenticular, p = polyhedral, s = spherical, o = oval, n = kidney-shaped, el = elliptical, si = simple, c = compound.

<sup>b</sup> Weight of swollen starch, based on its dry weight; loss of soluble polysaccharides is considered.

<sup>c</sup> Based on the sum of amylose and amylopectin.

<sup>d</sup> mg iodine/100 mg starch.

<sup>e</sup> Cleavage degree of polymerization, determined by degradation of branches with pullulanase or isoamylase.

<sup>f</sup> Tapioca.

<sup>g</sup> Millet.

<sup>h</sup> Pea.
changes occur starting at a certain temperature, which is characteristic of each type of starch (50–70 °C, cf. Table 4.24), called the gelatinization temperature. The starch granules absorb 20–40 g of water/g of starch, the viscosity of the suspension rising steeply. At the same time, a part of the amylose diffuses out of the granule and goes into solution. Finally, the granule bursts. In the first step of gelatinization, the starch crystallites melt and form a polymer network. This network breaks up at higher temperatures (ca. 100 °C), resulting in a solution of amylose and amylopectin. In gelatinization, water first diffuses into the granule, crystalline regions then melt with the help of hydration, and, finally, swelling gives rise to a solution through further diffusion of water. In this process, hydrogen bridges between glucose chains in the crystallites are primarily disrupted, and perhaps some of those in the amorphous regions as well. It is probable that the swelling of the amorphous regions facilitates the dissolving out of amylose from the crystallites, which are thereby destabilized. As with heating in water, the same effect occurs when starch is suspended in other solvents, e.g., liquid ammonia or dimethyl sulfoxide, or mechanically damaged, e.g., by dry grinding.

The course of gelatinization depends not only on the botanical origin of the starch and the temperature used, but also on the water content of the suspension (Fig. 4.27). Thus, dried starch with 1–3% of water undergoes only slight changes up to a temperature of 180 °C, whereas starch with 60% of water completely gelatinizes at temperatures as low as 70 °C.

If an aqueous starch suspension is maintained for some time at temperatures below the gelatinization temperature, a process known as tempering, the gelatinization temperature is increased, apparently due to the reorganization of the structure of the granule. Treatment of starch at low water contents and higher temperatures results in the stabilization of the crystallites and, consequently, a decrease in the swelling capacity. Figure 4.28 shows the resulting change in the X-ray diffraction spectrum from type B to type A, using potato starch as an example.

The changes in the physical properties caused by treating processes of this type can, however, vary considerably, depending on the botanical origin of the starches. This is shown in Table 4.25 for potato and wheat starch. On wet heating, the swelling capacity of both starches decreases, although to different extents. On the other hand, there is a decrease in solubility only of
Table 4.25. Physicochemical properties of starches before (1) and after (2) heat treatment in the wet state ($T = 100 \, ^\circ C, t = 16 \, h, H_2O = 27\%$)

<table>
<thead>
<tr>
<th>Property</th>
<th>Wheat starch 1</th>
<th>Wheat starch 2</th>
<th>Potato starch 1</th>
<th>Potato starch 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start of gelatinization ($^\circ C$)</td>
<td>56.5</td>
<td>61</td>
<td>60</td>
<td>60.5</td>
</tr>
<tr>
<td>End of gelatinization ($^\circ C$)</td>
<td>62</td>
<td>74</td>
<td>68</td>
<td>79</td>
</tr>
<tr>
<td>Swelling capacity at $80 , ^\circ C$ (ratio)</td>
<td>7.15</td>
<td>5.94</td>
<td>62.30</td>
<td>19.05</td>
</tr>
<tr>
<td>Solubility at $80 , ^\circ C$ (%)</td>
<td>2.59</td>
<td>5.93</td>
<td>31.00</td>
<td>10.10</td>
</tr>
<tr>
<td>Water binding capacity (%)</td>
<td>89.1</td>
<td>182.6</td>
<td>102.00</td>
<td>108.7</td>
</tr>
<tr>
<td>Enzymatic vulnerability (% dissolved)</td>
<td>0.44</td>
<td>48.55</td>
<td>0.57</td>
<td>40.35</td>
</tr>
</tbody>
</table>

Fig. 4.27. Gelatinization temperature of differently hydrated starches (— potato starch, −···−··· wheat starch, determined by differential thermal analysis, differential calorimetry, and double refraction) (according to Galliard, 1987)

potato starch, while that of wheat starch clearly increases. The explanation put forward to explain these findings is that the amorphous amylose of potato starch is converted to an ordered, less soluble state, while the amylose of cereal starch, present partially in the form of helices with enclosed lipids, changes into a more easily leachable state.

A gelatinization curve for potato starch is presented in Fig. 4.29. The number of gelatinized starch granules was determined by microscopy. Another way to monitor gelatinization as a function of temperature is to measure the viscosity of a starch suspension. The viscosity curves in Fig. 4.30 show that, as mentioned above, the viscosity initially increases due to starch granule swelling. The subsequent disintegration of the swollen granule is accompanied by a drop in viscosity. The shape of the curve varies greatly for different starches.

Fig. 4.28. X-ray diffraction diagrams of potato starch before (1) and after (2) thermal treatment ($102 \, ^\circ C/16 \, h$) at a water content of 40%. The pattern of native starch (18.3% of water) corresponds to the B-type and that of treated starch (24.2% of water) to the A-type (according to Galliard, 1987)

Potato starch shows a very high maximum ($\sim 4000$ Brabender units), followed by a steep drop. Waxy corn starch exhibits similar behavior, except that the maximum is not as high. In normal corn starch, the maximum is still lower, but the following drop is slight, i.e., the granules are more stable. Under these conditions, amylomaize starch does not swell, even though ca. 35% of
the amylose goes into solution. The viscosity of a starch paste generally increases on rapid cooling with mixing, while a starch gel is formed on rapid cooling without mixing.

Amylose gels tend to retrograde. This term denotes the largely irreversible transition from the solubilized or highly swollen state to an insoluble, shrunken, microcrystalline state (Fig. 4.31). This state can also be directly achieved by slowly cooling a starch paste. The tendency towards retrogradation is enhanced at low temperatures, especially near 0°C, neutral pH values, high concentration, and by the absence of surface active agents. It also depends on the molecular weight and on the type of starch, e.g., it increases in the series potato < corn < wheat. The transitions described from very water-deficient starting states via very highly swollen states or solutions to more or less shrunken states are linked to changes in the interactions between the glucans and to conformational changes. At present, these changes cannot be fully described because they greatly depend on the conditions in each case, e.g., even on the presence of low molecular compounds.

It is known that the gelatinization temperature is increased by polyhydroxy compounds (glycerol, sugar) and decreased by salts (NaCl, CaCl₂), as presented in Fig. 4.32 (top) as a function of water activity, which is lowered by the dissolved substances (aw, cf. 0.3.1). Apart from the activity of the solvent water, if its volume fraction (ν₁), which changes in reverse order to the volume fraction of the solute, is considered and if the gelatinization temperature is plotted against ln aw/V₁, instead of aw, the effect of the different dissolved substances is unified (Fig. 4.32, bottom). The reason is that polyhydroxy compounds cause a large change in νₑ and a small change in aw, while a small change in νₑ is linked to a large change in aw in the case of the salts.

Lipids also influence the properties of starch. Like free amino acids, monoglycerides or fatty acid esters of hydroxy acids, lipids form inclusion compounds with amylose (cf. 4.4.4.14.3). Like di- and triglycerides, they also reduce the swelling capacity and solubility by inhibiting water diffusion. Therefore, both degreasing as well as lipid addition are of importance as physical modification methods of starches.
4.4 Polysaccharides

4.4.4.14.3 Structure and Properties of Amylose

Amylose is a chain polymer of $\alpha$-D-glucopyranosyl residues linked $1 \rightarrow 4$:

Enzymatic hydrolysis of the chain is achieved by $\alpha$-amylase, $\beta$-amylase and glucoamylase. Often, $\beta$-amylase does not degrade the molecule completely into maltose, since a very low branching is found along the chain with $\alpha(1 \rightarrow 6)$ linkages. The molecular size of amylose is variable. The polymerization degree in wheat starch lies between 500 and 6000, while in potatoes it can rise up to 4500. This corresponds to a molecular weight of 150–750 kdal. X-ray diffraction experiments conducted on oriented amylose fibers make possible the assignment of the types of starch mentioned above to definite molecular structural elements. Oriented fibers of the A-type were obtained by cutting and stretching thin films of acetylamylose at 150 °C, deacetylation in alcoholic alkali, and conditioning at 80% relative air humidity and 85 °C. Type B fibers were obtained in a corresponding manner by conditioning the deacetylated material at room temperature for three days at 80% and for another three days at 100% relative air humidity, followed by aftertreatment in water at 90 °C for 1 h. The diffraction patterns obtained with these oriented fibers corresponded to those of types A and B given by native starch powders, allowing the development of structural models.

The structural elements of type B are left-hand double helices (Fig. 4.34a), which are packed in a parallel arrangement (Fig. 4.33). One turn of the double helix is 2.1 nm long, which corresponds to 6 glucose residues, i.e., three residues from each glucan chain. Hydrogen bridges between the amylose molecules stabilize the double helix. The central channel surrounded by six double helices is filled with water (36 H$_2$O/unit cell). The A-type is very similar to the B-type, except that the central channel is occupied by another double helix, making the packing more close. In this type, only eight molecules of water per unit cell are inserted between the double helices. The transition from type B to type A achieved by wet heating has been described already (4.4.4.14.2, Fig. 4.28). It is difficult to bring the postulated antiparallel arrangement of the double helices into line with the requirements of biosynthesis, where a parallel arrangement can be expected. It is possible that the present experimental data do not exclude such an arrangement.

Fig. 4.32. Gelatinization temperature of potato starch as a function of water activity $a_w$ (top) and of the natural logarithm of the quotient of activity $a_w$ to volume fraction $v_l$ of water (bottom); • glycerol, ○ maltose, □ saccharose, Δ glucose, ◊ ribose, ⊗ NaCl, ⊠ CaCl$_2$ (according to Galliard, 1987)
The double helix mentioned above and shown in Fig. 4.34 can, depending on conditions, change into other helical conformations. In the presence of KOH, for instance, a more extended helix results with 6 glucose residues per helical turn (Fig. 4.34, b) while, in the presence of KBr, the helix is even more stretched to 4 residues per turn (Fig. 4.34, c). Inclusion (clathrate) compounds are formed in the presence of small molecules and stabilize the V starch conformation (Fig. 4.34, d); it also has 6 glucose residues per helical turn. Stabilization may be achieved by H-bridges between O-2 and O-3 of neighboring residues within the same chain and between O-2 and O-6 of the residues \(i\) and \(i + 6\) neighbored on the helix surface. Many molecules, such as iodine, fatty acids, fatty acid esters of hydroxyacarboxylic acids (e.g., stearyllactate), monoglycerides, phenols, arylhalogenides, n-butanol, t-butanol, and cyclohexane are capable of forming clathrate compounds with amylose molecules. The helix diameter, to a certain extent, conforms to the size of the enclosed guest molecule; it varies from 13.7 Å to 16.2 Å. While the iodine complex and that of n-butanol have 6 glucose residues per turn in a V conformation, in a complex with t-butanol the helix turn is enlarged to 7 glucose residues/turn (Fig. 4.34, e).

It is shown by an \(\alpha\)-naphthol clathrate that up to 8 residues are allowed (Fig. 4.34, f). Since the helix is internally hydrophobic, the enclosed “guest” also has to be lipophilic in nature. The enclosed molecule contributes significantly to the stability of a given conformation. For example, it is observed that the V conformation, after “guest” compound removal, slowly changes in a humid atmosphere to a more extended B conformation. Such a conformational transition also occurs during staling of bread or other bakery products. Freshly baked bread shows a V spectrum of gelatinized starch, but aged bread typically has the retrograded starch B spectrum. Figure 4.35 illustrates both conformations in the form of cylinder projections. While in V amylose, as already outlined, O-2 of residues \(i\) and O-6 of residues \(i + 6\) come into close contact through H-bridges, in the B pattern the inserted water molecules increase the double-strand distance along the axis of progression (h) from 0.8 nm for the V helix to 1 nm for the B helix.

Cereal starches are stabilized by the enclosed lipid molecules, so their swelling power is low. The swelling is improved in the presence of alcohols (ethanol, amyl alcohol, tert-amyl alcohol). Obviously, these alcohols are dislodging and removing the “guest” lipids from the helices.
4.4.4. Structure and Properties of Amylopectin

Amylopectin is a branched glucan with side chains attached in the 6-position of the glucose residues of the principal chain:

An average of 20–60 glucose residues are present in short chain branches and each of these
branch chains is joined by linkage of C-1 to C-6 of the next chain. The proposed structural models (Fig. 4.36) suggest that amylopectin also has double helices organized in parallel. As mentioned above, the main portion of a starch granule’s crystalline structure is apparently derived from amylopectin. The structural modell II in Fig. 4.36 clearly shows from left to right the sequence of more compact (crystalline) and less compact (amorphous) sections. In this model, a distinction is made between shorter A-chains that are free of side chains and longer B chains that bear side chains. In the B chains, sections with compact successive side chains (cluster) alternate with branch-free sections.

The degree of polymerization of amylopectin (wheat) lies in the range of $3 \times 10^5$–$3 \times 10^6$ glucose units, which corresponds to a molecular mass of $5 \times 10^7$–$5 \times 10^8$. One phosphoric acid residue is found for an average of 400 glucose residues.

The organization of amylopectin molecules in starch granules is shown in Fig. 4.37: it is radial, the reducing end being directed outwards. Enzymatic degradation of amylopectin is similar to that of amylose. The enzyme β-amylase degrades the molecule up to the branching points. The remaining resistant core is designated as “limit-dextrin”.

Amylopectin, when heated in water, forms a transparent, highly viscous solution, which is ropy, sticky and coherent. Unlike with amylose, there is no tendency toward retrogradation. There are no staling or aging phenomena and no gelling, except at very high concentrations. However, there is a rapid viscosity drop in acidic media and on autoclaving or applying stronger mechanical shear force.

4.4.4.14.5 Utilization

Starch is an important thickening and binding agent and is used extensively in the production of puddings, soups, sauces, salad dressings, diet food preparations for infants, pastry filling, mayonnaise, etc. Corn starch is the main food starch and an important raw material for the isolation of starch syrup and glucose (cf. 19.1.4.3).

A layer of amylose can be used as a protecting cover for fruits (dates or figs) and dehydrated and candied fruits, preventing their sticking together. Amylose treatment of French fries decreases their susceptibility to oxidation. The good gelling property of a dispersable amylose makes it a suitable ingredient in instant puddings or sauces. Amylose films can be used for food packaging, as edible wrapping or tubing, as exemplified by a variety of instant coffee or tea products. Amylopectin utilization is also diversified. It is used to a large extent as a thickener or stabilizer.
Type IV, starch modified by the Maillard reaction or caramelization (formation of glycosidic bonds which are not hydrolyzed by α-amylase). Only amylose, and not amylopectin, is involved in Type III RS. The formation of RS depends on the temperature and on the water and lipid content. Indeed, 20% of RS is obtained on autoclaving corn starch. The yield can be raised to about 40% by heating under pressure and cooling (ca. 20 cycles). The optimal amylose/water ratio is 1:3.5 (g/g). Lipids complexed by amylose inhibit RS formation (cf. 15.2.4.1).

Type III RS consists of 60–70% of double helical α(1–4)polyglucan aggregates and only 25–30% of crystalline structures. It is assumed that the high content of the double helical conformation, which is similar to that of amylose type B, limits the activity of α-amylases. Various methods have been proposed for the determination of RS, e.g., RS equals total starch minus digestible starch. The results are only comparable if the incubation conditions and the α-amylases used correspond.

### 4.4.4.15 Modified Starches

Starch properties and those of amylose and amylopectin can be improved or “tailored” by physical and chemical methods to fit or adjust the properties to a particular application or food product.

#### 4.4.4.15.1 Mechanically Damaged Starches

When starch granules are damaged by grinding or by application of pressure at various water contents, the amorphous portion is increased, resulting in improved dispersibility and swellability in cold water, a decrease in the gelatinization temperature by 5–10 °C, and an increase in enzymatic vulnerability. In bread dough made from flour containing damaged starch, for instance, the uptake of water is faster and higher and amylose degradation greater.

#### 4.4.4.15.2 Extruded Starches

The X-ray diffraction diagram changes on extrusion of starch. The V-type appears first, followed
by its conversion to an E-type at higher temperatures (>185 °C), and reformation of the V-type on cooling. The E-type apparently differs from the V-type only in the spacing of the V helices of amylose.

Extruded starches are easily dispersible, better soluble, and have a lower viscosity. The partial degradation of appropriately heated amylose shows that chemical changes also occur at temperatures of 185–200 °C. Apart from maltose, isomaltose, gentiobiose, sophorose, and 1,6-anhydroglucopyranose appeared.

4.4.4.15.3 Dextrins

Heating of starch (<15% of water) to 100–200 °C with small amounts of acidic or basic catalysts causes more or less extensive degradation. White and yellow powders are obtained which deliver clear or turbid, highly sticky solutions of varying viscosity. These products are used as adhesives in sweets and as fat substitutes.

4.4.4.15.4 Pregelatinized Starch

Heating of starch suspensions, followed by drying, provides products that are swellable in cold water and form pastes or gels on heating. These products are used in instant foods, e.g., pudding, and as baking aids (cf. Table 4.26).

4.4.4.15.5 Thin-Boiling Starch

Partial acidic hydrolysis yields a starch product which is not very soluble in cold water but is readily soluble in boiling water. The solution has a lower viscosity than the untreated starch, and remains fluid after cooling. Retrogradation is slow. These starches are utilized as thickeners and as protective films (cf. Table 4.26).

4.4.4.15.6 Starch Ethers

When a 30–40% starch suspension is reacted with ethylene oxide or propylene oxide in the presence of hydroxides of alkali and/or alkali earth met-

als (pH 11–13), hydroxyethyl- or hydroxypropyl-
derivatives are obtained (R′ = H, CH3):

\[
\begin{align*}
R-OH + \overset{\text{OH}}{\text{R'}} & \rightarrow R-O-CH_2-CHR' \\
\text{(4.151)}
\end{align*}
\]

The derivatives are also obtained in reaction with the corresponding epichlorohydrins. The substitution degree can be controlled over a wide range by adjusting process parameters. Low substitution products contain up to 0.1 mole alkyl group/mole glucose, while those with high substitution degree have 0.8–1 mole/mole glucose. Introduction of hydroxyalkyl groups, often in combination with a small extent of cross-linking (see below) greatly improves starch swelling power and solubility, lowers the gelatinization temperature and substantially increases the freeze–thaw stability and the paste clarity of highly-viscous solutions. Therefore, these products are utilized as thickeners for refrigerated foods (apple and cherry pie fillings, etc), and heat-sterilized canned food (cf. Table 4.26).

Reaction of starch with monochloroacetic acid in an alkaline solution yields carboxymethyl starch:

\[
\begin{align*}
R-OH + \overset{\text{OH}}{\text{CH_2COO}} & \rightarrow R-O-CH_2-COO \overset{\text{OH}}{\text{}} \\
\text{(4.152)}
\end{align*}
\]

These products swell instantly, even in cold water and in ethanol. Dispersions of 1–3% carboxymethyl starch have an ointment–like (pomade) consistency, whereas 3–4% dispersions provide a gel-like consistency. These products are of interest as thickeners and gelling agents.

4.4.4.15.7 Starch Esters

Starch monophosphate ester is produced by dry heating of starch with alkaline orthophosphate or alkaline tripolyphosphate at 120–175 °C:

\[
\begin{align*}
R-OH + \overset{\text{OH}}{\text{POCl_3/Alkali phosphate}} & \rightarrow R-OPO_2H \overset{\text{OH}}{\text{}} \\
\text{(4.153)}
\end{align*}
\]

Starch organic acid esters, such as those of acetic acid, longer chain fatty acids (C₆–C₂₆), succinic,
adipic or citric acids, are obtained in reactions with the reactive derivatives (e.g., vinyl acetate) or by heating the starch with free acids or their salts. The thickening and paste clarity properties of the esterified starch are better than in the corresponding native starch.

In addition, esterified starch has an improved freeze–thaw stability. These starches are utilized as thickeners and stabilizers in bakery products, soup powders, sauces, puddings, refrigerated food, heat-sterilized canned food and in margarines. The starch esters are also suitable as protective coatings, e.g., for dehydrated fruits or for aroma trapping or encapsulation (cf. Table 4.26).

4.4.4.15.8 Cross-Linked Starches

Cross-linked starches are obtained by the reaction of starch (R–OH) with bi- or polyfunctional reagents, such as sodium trimetaphosphate, phosphorus oxychloride, epichlorohydrin or mixed anhydrides of acetic and dicarboxylic acids (e.g., adipic acid):

\[
2 \text{R–OH} + \text{R}’\text{CO}–\text{O–CO–(CH}_3\text{)}_n\text{CO–O–COR}’ \rightarrow \text{R–CO–(CH}_3\text{)}_n\text{CO–O–COR}’ (4.154)
\]

The starch granule gelatinization temperature increases in proportion to the extent of cross-linking, while the swelling power decreases (Fig. 4.38). Starch stability remains high at extreme pH values (as in the presence of food acids) and under conditions of shear force. Cross-linked starch derivatives are generally used when high starch stability is demanded.

4.4.4.15.9 Oxidized Starches

Starch hydrolysis and oxidation occur when aqueous starch suspensions are treated with sodium hypochlorite at a temperature below the starch gelatinization temperature range. The products obtained have an average of one carboxyl group per 25–50 glucose residues:

\[
\begin{align*}
\text{O–OH} & \rightarrow \text{R–O–CH}_2\text{CH–CH}_2\text{Cl} \\
\text{OH} & \rightarrow \text{R–O–CH}_2\text{CH–CH}_2\text{Cl} \\
\text{ROH} & \rightarrow \text{R–O–CH}_2\text{CH–CH}_2\text{O–R} \\
2 \text{R–OH} & \rightarrow (\text{NaPO}_3)_2 \rightarrow \text{R–O–PO–R} (4.155)
\end{align*}
\]

Oxidized starch is used as a lower-viscosity filler for salad dressings and mayonnaise. Unlike thin-boiling starch, oxidized starch does not retrograde nor does it set to an opaque gel.

4.4.4.16 Cellulose

4.4.4.16.1 Occurrence, Isolation

Cellulose is the main constituent of plant cell walls, where it usually occurs together with hemicelluloses, pectin and lignin. Since cellulase enzymes are absent in the human digestive tract, cellulose, together with some other inert polysaccharides, constitute the indigestible carbohydrate of plant food (vegetables, fruits or cereals), referred to as dietary fiber. Cellulases are also absent in the digestive tract of animals, but herbivorous an-
animals can utilize cellulose because of the rumen microflora (which hydrolyze the cellulose). The importance of dietary fiber in human nutrition appears mostly to be the maintenance of intestinal motility (peristalsis).

4.4.4.16.2 Structure, Properties

Cellulose consists of $\beta$-glucopyranosyl residues joined by $1 \rightarrow 4$ linkages (cf. Formula 4.158). Cellulose crystallizes as monoclinic, rod-like crystals. The chains are oriented parallel to the fiber direction and form the long b-axis of the unit cell (Fig. 4.39). The chains are probably somewhat pleated to allow intrachain hydrogen bridge formation between O-4 and O-6, and between O-3 and O-5 (cf. Formula 4.159). Intermolecular hydrogen bridges (stabilizing the parallel chains) are present in the direction of the a-axis while hydrophobic interactions exist in the c-axis direction. The crystalline sections comprise an average of 60% of native cellulose. These sections are interrupted by amorphous gel regions, which can become crystalline when moisture is removed. The acid- or alkali-labile bonds also apparently occur in these regions. Microcrystalline cellulose is formed when these bonds are hydrolyzed. This partially depolymerized cellulose product with a molecular weight of 30–50 kdal, is still water insoluble, but does not have a fibrose structure. Cellulose has a variable degree of polymerization (denoted as DP; number of glucose residues per chain) depending on its origin. The DP can range from 1000 to 14,000 (with corresponding molecular weights of 162 to 2268 kdal). Because of its high molecular weight and crystalline structure, cellulose is insoluble in water. Also, its swelling power or ability to absorb water, which depends partly on the cellulose source, is poor or negligible.

4.4.4.16.3 Utilization

Microcrystalline cellulose is used in low-calorie food products and in salad dressings, desserts and ice creams. Its hydration capacity and dispersibility are substantially enhanced by adding it in combination with small amounts of carboxymethyl cellulose.

4.4.4.17 Cellulose Derivatives

Cellulose can be alkylated into a number of derivatives with good swelling properties and improved solubility. Such derivatives have a wide field of application.
4.4.17.1 Alkyl Cellulose, Hydroxyalkyl Cellulose

The reaction of cellulose with methylchloride or propylene oxide in the presence of a strong alkali introduces methyl or hydroxypropyl groups into cellulose (cf. Reaction 4.160). The degree of substitution (DS) is dependent on reaction conditions. Mixed substituted products are also produced, e.g., methylhydroxypropyl cellulose or methylethyl cellulose. The substituents interfere with the normal crystalline packing of the cellulose chains, thus facilitating chain solvation. Depending on the nature of the substituent (methyl, ethyl, hydroxymethyl, hydroxyethyl or hydroxypropyl) and the substitution degree, products are obtained with variable swelling powers and water solubilities. A characteristic property for methyl cellulose and double-derivatized methylhydroxypropyl cellulose is their initial viscosity drop with rising temperature, setting to a gel at a specific temperature. Gel setting is reversible. Gelling temperature is dependent on substitution type and degree. Figure 4.40 shows the dependence of gelling temperature on the type of substitution and the concentration of the derivatives in water. Hydroxyethyl substituents stabilize the hydration layer around the macromolecule and, thereby, increase the gelling temperature. Changing the proportion of methyl to hydroxypropyl substituents can vary the jelling temperature within a wide range.

The above properties of cellulose derivatives permit their diversified application (Table 4.27). In baked products obtained from gluten-poor or gluten-free flours, such as those of rice, corn or rye, the presence of methyl and methylhydroxypropyl celluloses decreases the crumbliness and friability of the product, enables a larger volume of water to be worked into the dough and, thus, improves the extent of starch swelling during oven baking. Since differently substituted celluloses offer a large choice of gelling temperatures, each application can be met by using the most suitable derivative. Their addition to batter or a coating mix for meats (panure) decreases oil uptake in frying. Their addition to dehydrated fruits and vegetables improves rehydration characteristics and texture upon reconstitution. Sensitive foods can be preserved by applying alkyl cellulose as a protective coating or film. Cellulose derivatives can also be used as thickening agents in low calorie diet foods. Hydroxypropyl cellulose is a powerful emulsion stabilizer, while methylethyl cellulose has the property of a whipping cream: it can be whipped into a stable foam consistency.

4.4.17.2 Carboxymethyl Cellulose

Carboxymethyl cellulose is obtained by treating alkaline cellulose with chloroacetic acid.
Table 4.27. Utilization of cellulose derivatives (in amounts of 0.01 to 0.8%)

<table>
<thead>
<tr>
<th>Food product</th>
<th>Cellulose derivative&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Effect &lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 2 3</td>
<td>A B C D E F G H I</td>
</tr>
<tr>
<td>Baked products</td>
<td>+ + +</td>
<td>+ + + + +</td>
</tr>
<tr>
<td>Potato products</td>
<td>+ +</td>
<td>+ + + + +</td>
</tr>
<tr>
<td>Meat and fish</td>
<td>+ +</td>
<td>+ + + +</td>
</tr>
<tr>
<td>Mayonnaise, dressings</td>
<td>+ +</td>
<td>+ + +</td>
</tr>
<tr>
<td>Fruit jellies</td>
<td>+</td>
<td>+ + +</td>
</tr>
<tr>
<td>Fruit juices</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Brewery</td>
<td>+ +</td>
<td>+ +</td>
</tr>
<tr>
<td>Wine</td>
<td>+ +</td>
<td>+ +</td>
</tr>
<tr>
<td>Ice cream, cookies</td>
<td>+ +</td>
<td>+ + +</td>
</tr>
<tr>
<td>Diet food</td>
<td>+ +</td>
<td>+</td>
</tr>
</tbody>
</table>

<sup>a</sup> 1: Carboxymethyl cellulose, Na-salt; 2: methyl cellulose; 3: hydroxypropyl methyl cellulose.

<sup>b</sup> A: Thickening effect; B: water binding/holding; C: cold gel setting; D: gel setting at higher temperatures; E: emulsifier; F: suspending effect; G: surface activity; H: adsorption; and I: film-forming property.

The properties of the product depend on the degree of substitution (DS; 0.3–0.9) and of polymerization (DP; 500–2000). Low substitution types (DS ≤ 0.3) are insoluble in water but soluble in alkali, whereas higher DS types (>0.4) are water soluble. Solubility and viscosity are dependent on pH.

Carboxymethyl cellulose is an inert binding and thickening agent used to adjust or improve the texture of many food products, such as jellies, paste fillings, spreadable process cheeses, salad dressings and cake fillings and icings (Table 4.27). It retards ice crystal formation in ice cream, stabilizing the smooth and soft texture. It retards undesired saccharose crystallization in candy manufacturing and inhibits starch retrogradation or the undesired staling in baked goods. Lastly, Carboxymethyl cellulose improves the stability and rehydration characteristics of many dehydrated food products.

### 4.4.18 Hemicelluloses

The term hemicelluloses refers to substances which occupy the spaces between the cellulose fibrils within the cell walls of plants. Various studies, e.g., on apples, potatoes, and beans, show that xyloglucans dominate in the class *Dicotyledoneae*. A section of the structure of a xyloglucan from runner beans is presented in Formula 4.161.

In the class *Monocotyledoneae*, the composition of the hemicelluloses in the endosperm tissue varies greatly, e.g., wheat and rye contain mainly arabinoxylans (pentosans, cf. 15.2.4.2.1), while β-glucans (cf. 15.2.4.2.2) predominate in barley and oats.

![Formula 4.161](4.161)
4.4.4.19 Xanthan Gum

4.4.4.19.1 Occurrence, Isolation

Xanthan gum, the extracellular polysaccharide from *Xanthomonas campestris* and some related microorganisms, is produced on a nutritive medium containing glucose, NH₄Cl, a mixture of amino acids, and minerals. The polysaccharide is recovered from the medium by isopropanol precipitation in the presence of KCl.

4.4.4.19.2 Structure, Properties

Xanthan gum can be regarded as a cellulose derivative. The main chain consists of 1,4 linked β-glucopyranose residues. On an average, every second glucose residue bears in the 3-position a trisaccharide of the structure \( \beta-D-Manp-(1 \rightarrow 4)\beta-D-GlcPA(1 \rightarrow 2)\alpha-D-Manp \) as the side chain. The mannose bound to the main chain is acetylated in position 6 and ca. 50% of the terminal mannose residues occur ketalized with pyruvate as 4,6-O-(1-carboxyethylidene)-D-mannopyranose (cf. Formula 4.162; GlcpA: glucuronic acid).

![Formula 4.162](image)

The molecular weight of xanthan gum is >\( 10^6 \) dal. In spite of this weight, it is quite soluble in water. The highly viscous solution exhibits a pseudoplastic behavior (Fig. 4.41). The viscosity is to a great extent, independent of temperature. Solutions, emulsions and gels, in the presence of xanthan gums, acquire a high freeze-thaw stability.

4.4.4.19.3 Utilization

The practical importance of xanthan gum is based on its emulsion-stabilizing and particle-suspending abilities (turbidity problems, essential oil emulsions in beverages). Due to its high thermal stability, it is useful as a thickening agent in food canning. Xanthan gum addition to starch gels substantially improves their freeze-thaw stability.

Xanthan gum properties might also be utilized in instant puddings: a mixture of locust bean flour, Na-pyrophosphate and milk powder with xanthan gum as an additive provides instant jelly after reconstitution in water. The pseudoplastic thixotropic properties, due to intermolecular association of single-stranded xanthan gum molecules, are of interest in the production of salad dressings, i.e. a high viscosity in the absence of a shear force and a drop in viscosity to a fluid state under a shear force.

4.4.4.20 Scleroglucan

4.4.4.20.1 Occurrence, Isolation

*Sclerotium* species, e.g., *S. glucanicum*, produce scleroglucan on a nutritive medium of glucose, nitrate as N-source and minerals. The polysaccharide is recovered from the nutritive medium by alcoholic precipitation.

4.4.4.20.2 Structure, Properties

The “backbone” of scleroglucan is a \( \beta-1,3 \)-glucan chain that, on an average, has an attached glucose
as a side chain on every third sugar residue (cf. Formula 4.163).

\[ \text{Formula 4.163} \]

The polysaccharide has a molecular weight of about 130 kdal and is very soluble in water. Solutions have high viscosities and exhibit pseudo-plastic thixotropic properties.

4.4.4.20.3 Utilization

Scleroglucan is used as a food thickener and, on the basis of its good film-forming property, is applied as a protective coating to dried foods.

4.4.4.21 Dextran

4.4.4.21.1 Occurrence

*Leuconostoc mesenteroides, Streptobacterium dextranicum, Streptococcus mutans* and some other bacteria produce extracellular dextran from saccharose with the help of \( \alpha \)-1,6-glucan: D-fructose-2-glucosyl transferase (dextran sucrase, EC 2.4.1.5).

4.4.4.21.2 Structure, Properties

Dextran is an \( \alpha \)-1,6-glucan (Formula 4.164; molecular weight \( M_r = 4-5 \times 10^7 \) dal) with several glucose side chains, which are bound to the main chain of the macromolecule primarily through 1,3-linkages but, in part, also by 1,4- and 1,2-linkages. On an average, 95% of the glucose residues are present in the main chain. Dextran is very soluble in water.

\[ \text{Formula 4.164} \]

4.4.4.21.3 Utilization

Dextran is used mostly in medicine as a blood substitute. In the food industry it is used as a thickening and stabilizing agent, as exemplified by its use in baking products, confections, beverages and in the production of ice creams.

4.4.4.22 Inulin and Oligofructose

4.4.4.22.1 Occurrence

Inulin occurs as a reserve carbohydrate in many plant families, e.g., scorzonera, topinambur, chicory, rye, onion and dahlia bulb.

4.4.4.22.2 Structure

Inulin contains about 30 furanoid D-fructose units in a \( \beta \)-1,2-linkage. This linear polysaccharide has \( \alpha \)-glucose residues in 2,1-bonding at its ends. Individual \( \alpha \)-glucose residues in 1,3-bonding have also been detected in the interior of the polysaccharide. Inulin (M, 5000–6000) is soluble in warm water and resistant to alkali.

4.4.4.22.3 Utilization

Inulin is nondigestible in the small intestine, but is degraded by the bacteria in the large intestine. It can be used in many foods as a sugar and fat substitute (cf. 8.16.1.2), e.g., biscuits, yoghurt, desserts and sweets. Inulin yields D-fructose on acid or enzymatic hydrolysis. Oligofructans have a slightly sweet taste due to the lower degree of polymerization.
4.4.4.23 Polyvinyl Pyrrolidone (PVP)

4.4.4.23.1 Structure, Properties

This compound is used as if it were a polysaccharide-type additive. Therefore, it is described here. The molecular weight of PVP can range from 10–360 kdal.

\[ \text{(4.165)} \]

It is quite soluble in water and organic solvents. The viscosity of the solution is related to the molecular weight.

4.4.4.23.2 Utilization

PVP forms insoluble complexes with phenolic compounds and, therefore, is applied as a clarifying agent in the beverage industry (beer, wine, fruit juice). Furthermore, it serves as a binding and thickening agent, and as a stabilizer, e.g., of vitamin preparations. Its tendency to form films is utilized in protective food films (particle solubility enhancement and aroma fixation in instant tea and coffee production).

4.4.5 Enzymatic Degradation of Polysaccharides

Enzymes that cleave polysaccharides are of interest for plant foods. Examples are processes that occur in the ripening of fruit (cf. 18.1.3.3.2), in the processing of flour to cakes and pastries (cf. 15.2.2.1), and in the degradation of cereals in preparation for alcoholic fermentation (cf. 20.1.4). In addition, enzymes of this type are used in food technology (cf. 2.7.2.2) and in carbohydrate analysis (cf. Table 2.16 and 4.4.6). The following hydrolases are of special importance.

4.4.5.1 Amylases

Amylases hydrolyze the polysaccharides of starch.

4.4.5.1.1 \(\alpha\)-Amylase

\(\alpha\)-Amylase hydrolyzes starch, glycogen, and other 1,4-\(\alpha\)-glucans. The attack occurs inside the molecule, i.e., this enzyme is comparable to endopeptidases. Oligosaccharides of 6–7 glucose units are released from amylose. The enzyme apparently attacks the molecule at the amylose helix (cf. 4.4.4.14.3) and hydrolyzes “neighboring” glycoside bonds that are one turn removed. Amylopectin is cleaved at random; the branch points (cf. 4.4.4.14.4) are overjumped. \(\alpha\)-Amylase is activated by \(\text{Ca}^{2+}\) ions (cf. 2.3.3.1 and 2.7.2.2.2).

The viscosity of a starch solution rapidly decreases on hydrolysis by \(\alpha\)-amylase (starch liquefaction) and the iodine color disappears. The dextrins formed at first are further degraded on longer incubation, reducing sugars appear and, finally, \(\alpha\)-maltose is formed. The activity of the enzyme decreases rapidly with decreasing degree of polymerization of the substrate.

Catalysis is accelerated by the gelatinization of starch (cf. 4.4.4.14.2). For example, the swollen substrate is degraded 300 times faster by a bacterial amylase and \(10^5\) times faster by a fungal amylase than is native starch.

4.4.5.1.2 \(\beta\)-Amylase

This enzyme catalyzes the hydrolysis of 1,4-\(\alpha\)-D-glucosidic bonds in polysaccharides (mechanism, 2.4.2.5), effecting successive removals of maltose units from the nonreducing end. Hydrolysis is linked to a Walden inversion at C-1, giving rise to \(\beta\)-maltose. This inversion, which can be detected polarimetrically, represents a definite characteristic of an exoglycanase.

In contrast to amylose, amylopectin is not completely hydrolyzed. All reaction stops even before branch points are reached.

4.4.5.1.3 Glucan-1,4-\(\alpha\)-D-glucosidase (Glucoamylase)

This glucoamylase starts at the nonreducing end of 1,4-\(\alpha\)-D-glucans and successively liberates \(\beta\)-D-glucose units. In amylopectin, \(\alpha\)-1,6-branches are cleaved ca. 30 times slower than \(\alpha\)-1,4-bonds.
4.4.5.1.4 α-Dextrin Endo-1,6-α-glucosidase (Pullulanase)

This enzyme hydrolyzes 1,6-α-D-glucosidic bonds in polysaccharides, e.g., in amylopectin, glycogen, and pullulan. Linear amylase fragments are formed from amylopectin.

4.4.5.2 Pectinolytic Enzymes

Pectins (cf. 4.4.4.13) in plant foods are attacked by a series of enzymes. A distinction is made between:

- Pectin esterases which occur widely in plants and microorganisms and demethylate pectin to pectic acid (Formula 4.166).
- Enzymes which attack the glycosidic bond in polygalacturonides (Table 4.28). These include hydrolases and lyases which catalyze a transelimination reaction (see Formula 4.167). The double bond formed in the product of the last mentioned reaction results in an increase in the absorption at 235 nm.

The second group can be further subdivided according to the substrate (pectin or pectic acid) and to the site of attack (endo-/exo-enzyme), as shown in Table 4.28. The endo-enzymes strongly depolymerize and rapidly reduce the viscosity of a pectin solution.

<table>
<thead>
<tr>
<th>Enzyme</th>
<th>EC No.</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polygalacturonase</td>
<td>3.2.1.15</td>
<td>Pectin</td>
</tr>
<tr>
<td>Endo-polymethyl galacturonase</td>
<td></td>
<td>Pectic acid</td>
</tr>
<tr>
<td>Endo-polygalacturonase</td>
<td>3.2.1.67</td>
<td>Pectin</td>
</tr>
<tr>
<td>Exo-polygalacturonase</td>
<td></td>
<td>Pectic acid</td>
</tr>
<tr>
<td>Pectin lyase</td>
<td>4.2.2.10</td>
<td>Pectin</td>
</tr>
<tr>
<td>Endo-polymethyl galacturonlyase</td>
<td></td>
<td>Pectin</td>
</tr>
<tr>
<td>Pectate lyase</td>
<td>4.2.2.2</td>
<td>Pectic acid</td>
</tr>
<tr>
<td>Endo-polygalacturonate lyase</td>
<td>4.2.2.9</td>
<td>Pectic acid</td>
</tr>
<tr>
<td>Exo-polygalacturonate lyase</td>
<td></td>
<td>Pectic acid</td>
</tr>
</tbody>
</table>

Polygalacturonases occur in plants and microorganisms. They are activated by NaCl and some by Ca\(^{2+}\) ions as well. Pectin and pectate lyases are only produced by microorganisms. They are activated by Ca\(^{2+}\) ions and differ in the pH optimum (pH 8.5–9.5) from the polygalacturonases (pH 5–6.5).
4.4 Polysaccharides

4.4.5.3 Cellulases

Hydrolysis of completely insoluble, microcrystalline cellulose is a complicated process. For this purpose, certain microorganisms produce particles called cellusomes (particle weight ca. $10^6$). During isolation, these particles readily disintegrate into enzymes, which synergistically perform cellulose degradation, and components, which, among other things, support substrate binding. At least three enzymes are involved in the degradation of cellulose to cellobiose and glucose:

$$\text{Cellulose} \xrightarrow{C_1} \text{Cellobiose} \xrightarrow{\text{Cellobiase}} \text{Glucose}$$

As shown in Table 4.29, the $C_1$ and $C_x$ factors, which were found to be endo- and exo-1,4-$\beta$-glucanases respectively, hydrolyze cellulose to cellobiose. Since the $C_1$ factor is increasingly inhibited by its product, a cellobiase is needed so that cellulose breakdown is not rapidly brought to a standstill. However, cellobiase is also subject to product inhibition. Therefore, complete cellulose degradation is possible only if cellobiase is present in large excess or the glucose formed is quickly eliminated.

4.4.5.4 Endo-1,3(4)-$\beta$-glucanase

This hydrolase is also called laminarinase and hydrolyzes 1,3(4)-$\beta$-glucans. This enzyme occurs together with cellulases, e.g., in barley malt, and is involved in the degradation of $\beta$-glucans (cf. 15.2.4.2.2) in the production of beer.

4.4.5.5 Hemicellulases

The degradation of hemicelluloses also proceeds via endo- and exohydrolases. The substrate specificity depends on the monosaccharide building blocks and on the type of binding, e.g., endo-1,4-$\beta$-D-xylanase, endo-1,5-$\alpha$-L-arabinase. These enzymes occur in plants and microorganisms, frequently together with cellulases.

4.4.6 Analysis of Polysaccharides

The identification and quantitative determination of polysaccharides plays a role in the examination of thickening agents, balast material etc.

4.4.6.1 Thickening Agents

First, thickening agents must be concentrated. The process used for this purpose is to be modified depending on the composition of the food. In general, thickening agents are extracted from the defatted sample with hot water. Extracted starch is digested by enzymatic hydrolysis ($\alpha$-amylase, glucoamylase), and proteins are separated by precipitation (e.g., with sulfosalicylic acid). The polysaccharides remaining in the solution are separated with ethanol. An electropherogram of the polysaccharides dissolved in a borate buffer provides an initial survey of the thickening agents present. It is sometimes difficult to identify and, consequently, differentiate between the added polysaccharides and those that are endogenously present in many foods. In simple cases, it is sufficient if the electropherogram is supported by structural analysis. Here, the polysaccharides are permethylated (cf. 4.2.4.7), then subjected to acid hydrolysis, reduced with sodium borohydride (cf. 4.2.4.1) and converted to partially methylated alditol acetates by acetylation of the OH-groups (cf. 4.2.4.6).

These derivatives of the monosaccharide structural units are then qualitatively and quantitatively analyzed by gas chromatography on capillary columns. In more difficult cases, a preliminary separation of acidic and neutral polysaccharides on an ion exchanger is recommended. Methanolysis or hydrolysis of polysaccharides containing uronic acids and anhydro sugars are critical due to losses of these labile building blocks. Reductive cleavage of the permethylated polysaccharide is recommended as a gentle alternative to hydrolysis. In this process, partially methylated anhydroalditol acetates are formed as shown in Fig. 4.42, using a galactomannan as an example. Conclusions about the structure of the polysaccharide can be drawn from the result of the qualitative and quantitative analysis, which is carried out by gas chromatography/mass
Fig. 4.42. Reductive depolymerization of a permethylated galactomannan (according to Kiwitt-Haschemie et al., 1996) 1. Reductive cleavage with triethylsilane and trimethylsilylmethanesulfonate/boron trifluoride 2. Acetylation with acetic anhydride and N-methylimidazole

spectrometry. In the example presented here, the derivative 4-O-acetyl-1,5-anhydro-2,3,6-tri-O-methyl-D-mannitol (a in Fig. 4.42) results from the 1,4-linked D-mannose, the structural unit of the main chain. The derivative 4,6-di-O-acetyl-1,5-anhydro-2,3-di-O-methyl-D-mannitol (b) indicates the structural unit which forms the branch and the derivative 1,5-anhydro-2,3,4,6-tetra-O-methyl-D-galactitol (c) indicates the terminal D-galactopyranose of the side chain. The derivative 1,5-anhydro-2,3,4,6-tetra-O-methyl-D-mannitol (d) produced in small amounts shows the end of the main chain formed by D-mannopyranose. The appearance of glucose in the structural analysis indicates glucans or modified glucans, e.g., modified starches or cellulos. The identification of thickening agents of this type is achieved by the specific detection of the hetero-components, e.g., acetate or phosphate.

4.4.6.2 Dietary Fibers

Gravimetric methods are the methods of choice for the determination of dietary fibers (cf. 15.2.4.2). In the defatted sample, the digestible components (1,4-α-glucans, proteins) are enzymatically hydrolyzed (heat-stable α-amylase, glucoamylase, proteinase). After centrifugation,
<table>
<thead>
<tr>
<th>EC No.</th>
<th>Name</th>
<th>Synonym</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.1.4</td>
<td>Cellulase C&lt;sub&gt;x&lt;/sub&gt; factor</td>
<td>CMCCase&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Endohydrolysis of 1,4-β-D-glucosidic bonds</td>
</tr>
<tr>
<td></td>
<td></td>
<td>endo-1,4-β-glucanase</td>
<td></td>
</tr>
<tr>
<td>3.2.1.91</td>
<td>Cellulose</td>
<td>C&lt;sub&gt;1&lt;/sub&gt; factor</td>
<td>Exohydrolysis of 1,4-β-D-glucosidic bonds with formation of cellobiose from cellulose or 1,4-β-glucooligosaccharides. The attack proceeds from the nonreducing end.</td>
</tr>
<tr>
<td>1,4-β-cellobiosidase</td>
<td>avicellase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2.1.21</td>
<td>β-Glucosidase</td>
<td>Cellobiase amygdalase</td>
<td>Hydrolysis of terminal β-D-glucose residues in β-glucans</td>
</tr>
</tbody>
</table>

<sup>a</sup> CMC: carboxymethylcellulose; the enzyme activity can be measured via the decrease in viscosity of a CMC solution.

the insoluble fibers remain in the residue. The water soluble fibers in the supernatant are isolated by precipitation with ethanol, ultrafiltration or dialysis. The protein and mineral matter still remaining with the soluble and insoluble dietary fibers is deducted with the help of correction factors.

### 4.5 References


Ebert, G.: Biopolymere. Dr. Dietrich Steinkopff Verlag: Darmstadt. 1980


Hill, R.D., Munck, L. (Eds.): New approaches to research on cereal carbohydrates. Elsevier Science Publ.: Amsterdam. 1985