The Carbohydrates Found in Cereal Grains

The carbohydrates found in cereal grains may be categorised into five groups

- Mono- and di-saccharides
- Oligosaccharides
- Storage polysaccharides
- Cell wall storage polysaccharides
- Cell wall structural polysaccharides

Mono- and di-saccharides

Hexose monosaccharides (six carbon atoms) such as glucose and fructose are absorbed directly from the small intestine. The pentose monosaccharides, (five carbon atoms) D-xylose and L-arabinose, are also absorbed but urinary excretion of these sugars increases linearly as a percentage of intake as dietary concentration increased for chickens and pigs.

The common disaccharides found in plant material (sucrose, lactose, maltose, etc.), are hydrolysed to monosaccharides by enzymes secreted in the small intestine.

![Chemical structures of carbohydrates](image)

**Figure 1**  
Common monosaccharides

**Figure 2**  
Common disaccharides
2. Oligosaccharides

Oligosaccharides, especially the galacto-oligosaccharides, raffinose, stachyose and verbascose (figure 3) are present as carbohydrate reserves in many plant seeds. They are particularly prevalent in legume seeds such as soya but are also present in small quantities in cereals (0.5% DM in wheat, 0.3% in barley). They are readily fermented in the lower gut of monogastric animals by intestinal bacteria to yield volatile fatty acids and associated flatulent gases (carbon dioxide, methane and hydrogen). However, such fermentations are not of great benefit to the host animal and enzymes for digesting these oligosaccharides could be added to feed such that bird can utilise the constituent monosaccharides following hydrolysis.

Galp-α-1→6-Glup-β-1→2-Fruf \hspace{1cm} \text{Raffinose}

Galp-α-1→6-Galp-α-1→6-Glup-β-1→2-Fruf \hspace{1cm} \text{Stachyose}

Galp-α-1→6-Galp-α-1→6-Galp-α-1→6-Glup-β-1→2-Fruf \hspace{1cm} \text{Verbascose}

\textbf{Figure 3}
Structures of common galacto-oligosaccardies.

3. Storage polysaccharides (starch, fructans, etc.).

Starch is the main storage polysaccharide in most plants and is laid down in the form of insoluble starch granules whose main components are α-amylase and amyllopectin. α-amylase consists of linear chains of α-1, 4 linked glucose units (figure 4) whereas amyllopectin is heavily branched, the branch points being formed by α-1, 6 linkages (figures 5 and 6).

The α-amylase portion of starch is digested by α-amylases from pancreatic juice to maltose, maltotriose, and alpha limit dextrins. These are further hydrolysed to glucose by intestinally secreted maltases prior to absorption. Branched portions of amyllopectin are probably resistant to digestion by an α-amylase as an enzyme with α-1,6 degrading activity (pullulanase) will also be required.

\textbf{Figure 4}
A small section of α-amylase
4. Cell wall storage polysaccharides (mannans, galactans, xyloglucans, etc.).

The structure of the plant cell wall is extremely complex, containing many types of polysaccharide and structural proteins. Some of the polysaccharides are referred to as structural (see next section) whilst some, such as mannans, galactans and xyloglucans, are described as storage polysaccharides. The distinction between the two types is not very clear, however, the storage polysaccharides are the first carbohydrate reserves utilised when a dormant seed begins to germinate. Seeds with particularly high levels of these storage polysaccharides are not generally utilised in animal feeding and will not be discussed further.

5. Cell wall structural polysaccharides (cellulose, hemicellulose, pectins, etc.)

Cell wall polysaccharides play a vital role in maintaining the integrity of plant tissues. The plant cell wall is a biphasic structure in which highly ordered microfibrils of cellulose form a rigid skeleton. This is embedded in a gel like matrix composed of non-cellulosic polysaccharides (sometimes referred to as hemicellulose and pectin) and glycoproteins. As the plant tissue ages, lignin is laid down encrusting the microfibrils. In monocotyledonous plants the cellulose micro-fibrils are interlocked with glucurono-arabino-xylans, arabinoxylans and mixed linked β-glucans.

The type and level of non-cellulosic polysaccharides in the matrix of the cell wall can show considerable differences between plant species, between different cultivars of the same species and between the same cultivars grown and harvested under different climatic conditions or stages of maturity.

In the intact cell wall these non-cellulosic polysaccharides are insoluble. After extraction they become soluble hydrophilic molecules, indicating extensive cross linking between the polymers of the cell walls.

All of the sugars in structural plant cell wall polysaccharides are linked by types of glycosidic bonds which cannot be cleaved by endogenous avian or mammalian enzymes.
A proportion of the non-starch polysaccharide material associated with the endosperm cell walls of cereal grains is potentially soluble (Table 1). In the case of barley and oats, these soluble polysaccharides are mainly mixed linked β-glucans and in rye, triticale and wheat they are mainly arabinoxylans.

<table>
<thead>
<tr>
<th>Cereal</th>
<th>Arabinoxylan</th>
<th>β-Glucan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grain total</td>
<td>Grain soluble</td>
</tr>
<tr>
<td>Barley</td>
<td>56.9</td>
<td>4.8</td>
</tr>
<tr>
<td>Oats</td>
<td>76.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Rye</td>
<td>84.9</td>
<td>26.0</td>
</tr>
<tr>
<td>Wheat</td>
<td>66.3</td>
<td>11.8</td>
</tr>
</tbody>
</table>

**Table 1.**
The total and water-soluble arabinoxylan and β-glucan content of cereal grains (g/kg) and the percentage contribution of the arabinoxylan and β-glucan of starchy endosperm walls to the grain total.

**β-Glucans**

Cereal β-glucans are linear polymers of glucose with β-1 → 4 and β-1 → 3 glycosidic linkages, however, the exact molecular size and the proportion and distribution of the β-1 → 4 and β-1 → 3 linkages vary considerably. Most studies have been performed with barley β-glucan the majority of which consists of short regions (3 to 4 residues) of β-1 → 4 linkages interrupted by a single β-1 → 3 linkage (figure 7). Contiguous sequences of glucose residues linked by β-1 → 3 linkages occur rarely whereas certain regions may be linked by longer stretches of only β-1 → 4 linkages.

![Figure 7](image-url)

**Figure 7**
The structure of barley β-glucan. Note the 1→3 linkage between glucose residues 3 and 4.

The structure of cellulose is also β-1 → 4 linked glucose but without any β-1 → 3 linkages. It is the presence of these β-1 → 3 linkages in β-glucan which confers very different properties to cellulose and β-glucan, in particular, the β-glucan is soluble in water giving viscous solutions (figure 8) whereas cellulose is practically insoluble.
The enzymes responsible for breakdown of the two types of polysaccharide are also different such that β-glucanases (EC 3.2.1.6) are distinct enzymes from cellulases (EC 3.2.1.4). Whilst the exact catalytic mechanism of β-glucanase is unknown it is thought that the only bonds which are cleaved are the 1→4 bonds on the non-reducing side of the residue adjacent to a 1→3 bond (see figure 9). The complete three-dimensional structure of *Trichoderma* β-glucanase is shown in figure 10.

![Beta-glucan structure diagram](image)

**Figure 8**
The viscosity of β-glucan solutions.
Adapted from Lyons, T.P (1992) Feed Compounder 12, 22.

Where:

- G = -β-D-glucose p-(1→4)-
- G = -β-D-glucose p-(1→3)-

**Figure 9**
The main structural features of barley β-glucan and potential β-glucanase cleavage sites.
**Arabinoxylans**

Cereal arabinoxylans are complex molecules with a $\beta$-1, 4 linked xylose backbone and arabinose side chains. Two arabinoxylans occur in cereal grains, arabinoxylan I, consisting of a main chain of 4 linked $\beta$-D xylpyranosyl residues of which approximately half are substituted at the C3 position with $\alpha$-L-arabinofuranosyl residues. In arabinoxylan II, some of the xylose residues are substituted at both the C2 and C3 positions with $\alpha$-L-arabinofuranosyl residues (figure 11).

The structures below show the types of bond in the two forms of arabinoxylan. The actual molecules are very long, consisting of many thousand xylose residues. The pattern of substitution of arabinose sidechains is highly variable with some regions of the molecule being substituted whilst other regions are unsubstituted. Bengtsson *et al.*, 1992, found that the content of arabinoxylan II is more correlated to viscosity than arabinoxylan I.
Most fungal xylanases will only hydrolyse bonds in the arabinohylan backbone adjacent to residues which are not substituted (figure 12). Therefore, highly substituted structures such as arabinohylan I will not be degraded by xylanase alone and arabinohylan II will contain only a limited number of cleavage sites.

Where:

\[
\begin{align*}
\text{X} & = (\rightarrow 4)\-\beta-\text{D-xylose} - (1 \rightarrow) \\
\text{A} & = \text{arabinose} - (1 \rightarrow 3) \\
\end{align*}
\]

Figure 11
The structure of wheat type I and II arabinohylans.

Figure 12
The main structural features of wheat arabinohylan and potential xylanase cleavage sites
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