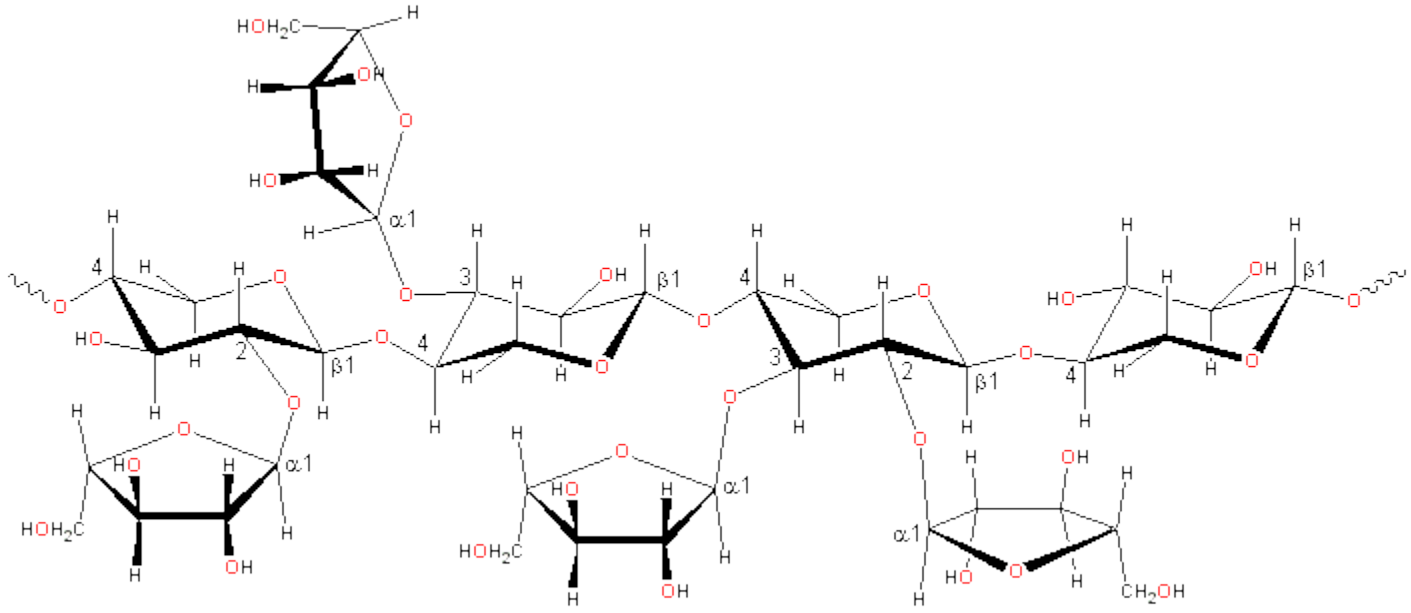
Arabinoxylan

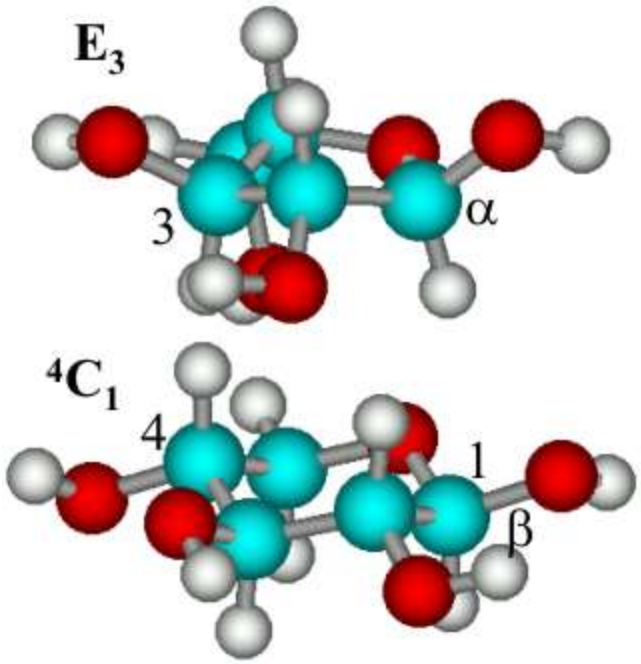
Source

Arabinoxylans are naturally found in the bran of grasses (*Graminiae*).

Structural unit



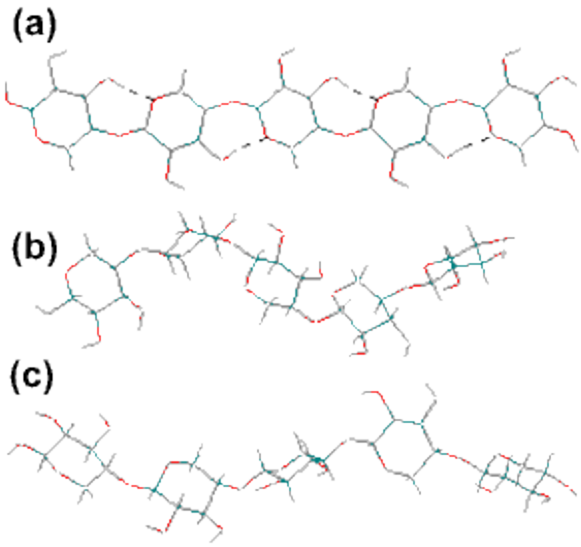
Arabinoxylans [230] consist of α-L-arabinofuranose residues attached as branch-points to β-(1⟶4)-linked D-xylopyranose polymeric backbone chains.[a] These may be 2- or 3-substituted or 2- and 3- di-substituted. In wheat flour, the distribution of the type of substitution is not random (contiguous similarly substituted residues being preferred due to the enzymatic mechanism) but the distribution of substituted (irrespective of of the substitution type) residues along the chain appears random [575]. The arabinose residues may also be linked to other groups attached such as glucuronic acid residues, ferulic acid crosslinks [1634] and acetyl groups [365].



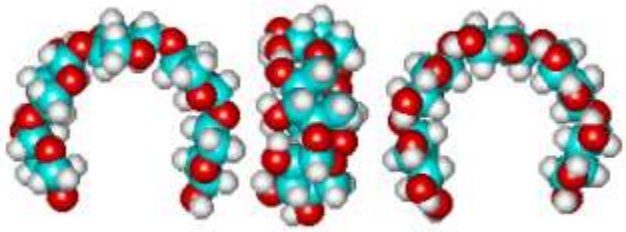
The most stable conformations of α-L-arabinofuranose (top) and β-(1⟶4)-linked D-xylopyranose residues. The furanose can, however, take up a number of other conformations with similar energy whereas the chair conformation of the pyranose residue is fixed.[b]

Molecular structure

Arabinoxylans generally consist of between 1500 - 5000 residues. Fiber studies indicate the molecules take up a twisted ribbon conformation with 3-fold symmetry. The free molecules in solution may, however, take up a wide variety of conformations with only moderately extended structures. Although the backbone xylan structure is similar to that occurring in cellulose there is little driving force to produce crystalline type structures as the intra- and inter-molecular hydrogen bonds associated with the 6-hydroxyl groups are necessarily absent. The presence of arabinose side chains reduce interaction between chains due to their inherently more flexible water-hungry furanose conformations. However, where there are sections of disubstituted xylan the chain is relatively inflexible and rod-like. Although relatively unsubstituted areas of the backbone may be able to interact as ribbons with themselves and β-glucans at higher temperatures such interactions are likely to be relatively weak and these areas are more likely to form helical entanglements. When the arabinose residues are stripped off the xylan backbone (using oxalic acid), aggregation appears at a Xyl/Ara ratio of about four and precipitation occurs when this is increased above ten [1387]. The loss of arabinose side chains also correlated with a loss in water binding capacity [1387].



Xylan backbone with φ_H ($H_1C_1OC_4$), ψ_H ($C_1OC_4H_4$) torsion angles of (a) 30°,-30°, (2_1 helix) similar to cellulose but unstable; (b) 57°,-141° (3_1 helix) forming a 3-fold right-handed helix; (c) 60°, 27° (3_1 helix) forming a 3-fold left-handed helix. A study using the MM3 force field gives the structures (a) and (c) as the most stable [920].



β-Xylan loop structure (φ_H ,ψ_H = 176°,3°) showing the hydrophobic cavity that may be produced as this link is the conformation of lowest potential energy. Such structuring will behave similar to the cyclodextrins in binding materials such as aroma compounds.

Functionality

Wheat and rye arabinoxylans are important functional ingredients in baked products affecting water binding and holding ,rheology and starch retrogradation. They also protect the gas retention in dough due to the viscous influence on gluten-starch films. Water binding is dependent on the arabinose substitution. Where this is absent the molecule binds less water and becomes less soluble but water is also lost from sections that are 2-. 3-disubstituted where there are steric exclusion

effects. Although there are some reports that the degree of arabinose substitution has little influence on the overall semi-flexible conformation (and hence the viscosity), it must influence areas within the structure and control over the radius of gyration may be lost due to the presence of under-substituted more-flexible regions. Entanglement of the hydrated chains increases the water-holding capacity of the arabinoxylans. The presence of oxidative ferulic acid cross-links increases the strength and permanence of this water-holding capacity and makes gels more elastic. The proportions of soluble and insoluble arabinoxylan has been proposed as a key feature in the function of the arabinoxylan [2016].

Interactive structures, including the diferulic acid link, are available (Jmol).

Source : http://www1.lsbu.ac.uk/water/hyara.html