

# Pectin

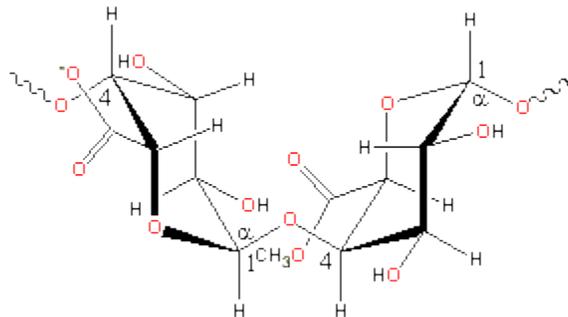
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## Pectin sources

Pectin ([E440](#)) is a heterogeneous grouping of acidic structural polysaccharides, found in fruit and vegetables (reviewed in [\[1581\]](#)) and mainly prepared from 'waste' citrus peel and apple pomace. It makes up between about 2% and 35% of plant cell walls [\[1680\]](#) and is important for plant growth, regulation of ion and water exchange, development and defense.

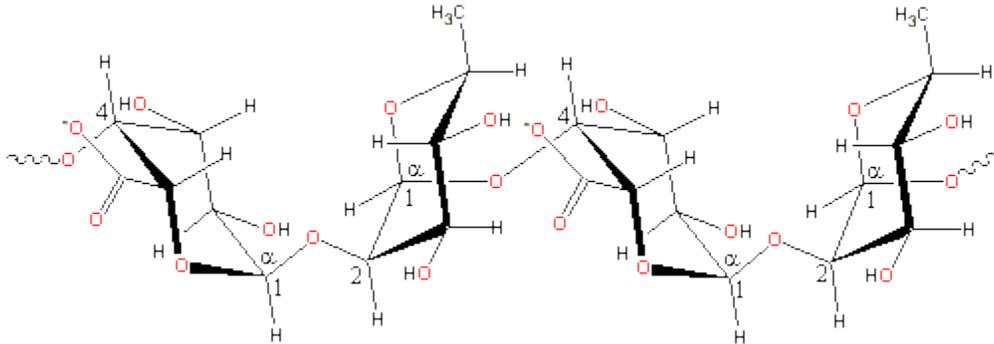
## Pectin structural unit

Pectin has a complex structure with an  $\alpha$ -(1 $\rightarrow$ 4)-linked D-galacturonic acid polysaccharide backbone. Preparations consist of substructural entities that depend on their source and extraction methodology. Commercial extraction causes extensive degradation of the neutral sugar-containing sidechains.



The majority of the structure consists of homopolymeric partially 6-methylated, and 2- and/or 3-acetylated poly- $\alpha$ -(1 $\rightarrow$ 4)-D-galacturonic acid residues ('smooth', see right) but there are substantial 'hairy' non-gelling areas (see below) of alternating  $\alpha$ -(1 $\rightarrow$ 2)-L-rhamnosyl- $\alpha$ -(1 $\rightarrow$ 4)-D-galacturonosyl sections containing branch-points with mostly neutral side chains (1 - 20 residues) of mainly  $\alpha$ -L-arabinofuranose and  $\alpha$ -D-galactopyranose (rhamnogalacturonan I). Also present from some sources are xylogalacturonan blocks of  $\alpha$ -(1 $\rightarrow$ 4)-D-galacturonic acid units, partially substituted at the O-3 position with single non-reducing  $\beta$ -D-xylopyranose and/or with longer (dimer to octamer)  $\beta$ -D-xylopyranose chains.

Pectins may also contain rhamnogalacturonan II sidechains containing other residues such as D-xylose, L-fucose, D-glucuronic acid, D-apiose, 3-deoxy-D-*manno*-2-octulosonic acid (Kdo) and 3-deoxy-D-*lyxo*-2-heptulosonic acid (Dha) attached to poly- $\alpha$ -(1 $\rightarrow$ 4)-D-galacturonic acid regions [478].



## Molecular structure

Generally, pectins do not possess exact structures [328]. Its structure and biosynthesis has been recently reviewed, with its biosynthesis requiring at least 67 transferases [1459]. D-galacturonic acid residues form most of the molecules, in blocks of 'smooth' and 'hairy' regions. The molecule does not adopt a straight conformation in solution, but is extended and curved ('worm like') with a large amount of flexibility. The 'hairy' regions of pectins are even more flexible and may have pendant arabinogalactans. The carboxylate groups tend to expand the structure of pectins as a result of their charge, unless they interact through divalent cationic bridging (their  $pK_a$  of about 2.9 [326] ensuring considerable negative charge under most circumstances). Methylation of these carboxylic acid groups forms their methyl esters, which take up a similar space but are much more hydrophobic and consequently have a different effect on the structuring of the surrounding water. The properties of pectins depend on the degree of esterification, which is normally about 70%. Low methoxyl-pectins (< 40% esterified) gel by calcium di-cation bridging between adjacent two-fold helical chains forming so-called 'egg-box' junction zone structures so long as a minimum of 14-20 residues can cooperate [326]. Gel strength increases with increasing  $Ca^{2+}$  concentration but reduces with temperature and acidity increase ( $pH < 3$ ) [463]. It may well be that the two carboxylate groups have to cooperate together in prizing the bound water away from the calcium ions to form the salt links that make up these junction zones. Low methoxyl pectin has a less demarked dimerization step than alginates, due to the random distribution of ester and amide groups along the pectin chain [1380]. The gelling ability of the di-cations is similar to that found with the alginates ( $Mg^{2+} \ll Ca^{2+}, Sr^{2+} < Ba^{2+}$ ) with  $Na^+$  and  $K^+$  not gelling. High methoxyl pectin shows a negligible dimerization upon binding with calcium due to the lack of sufficient carboxylate groups. If the methoxyl esterified content is greater than about 50%, calcium ions show some interaction but do not gel. The similarity to the behavior of the alginates is that poly- $\alpha$ -(1 $\rightarrow$ 4)-D-galacturonic acid is almost the mirror image of poly- $\alpha$ -(1 $\rightarrow$ 4)-L-guluronic acid, the only difference being that the 3-hydroxyl group is axial in the latter. The controlled removal of methoxyl groups, converting high methoxyl pectins to low-methoxyl pectins, is possible using pectin methylesterases but the reverse process is not easily achieved.

High methoxyl-pectins (> 43% esterified, usually ~67%) gel by the formation of hydrogen-bonding and hydrophobic interactions in the presence of acids (pH ~3.0, to reduce electrostatic repulsions) and sugars (for example, about 62% sucrose by weight, to reduce polymer-water interactions) [664]. Low methoxy-pectins (~35% esterified), in the absence of added cations, gel by the formation of cooperative 'zipped' associations at low temperatures (~10 °C) to form transparent gels [684]. This hydrogen-bonded association is likely to be similar to that of [alginate](#) (see above). The rheological properties of low methoxy-pectins are highly dependent on the salt cation, salt concentration and pH.

## Functionality

Pectins are mainly used as gelling agents, but can also act as thickener, [water binder](#) and stabilizer. Low methoxyl pectins (< 50% esterified) form thermoreversible gels in the presence of calcium ions and at low pH (3 - 4.5) whereas high methoxyl pectins rapidly form thermally irreversible gels in the presence of sufficient (for example, 65% by weight) sugars such as sucrose and at low pH (< 3.5); the lower the methoxyl content, the slower the set. The degree of esterification can be (incompletely) reduced using commercial pectin methyltransferase, leading to a higher viscosity and firmer gelling in the presence of Ca<sup>2+</sup> ions. Highly (2-O- and/or 3-O-galacturonic acid backbone) acetylated pectin from sugar beet is reported to gel poorly but have considerable emulsification ability due to its more hydrophobic nature, but this may be due to associated protein impurities [309].

As with other viscous polyanions such as [carrageenan](#), pectin may be protective towards milk casein colloids, enhancing the properties (foam stability, solubility, gelation and emulsification) of whey proteins whilst utilizing them as a source of calcium.

There is increasing evidence that dietary pectin may have some health benefits beyond its role as a useful dietary fiber. Small pectin fragments have a positive effect as an anti-cancer agent as they bind to and inhibit the various actions of the pro-metastatic protein galectin-3 [1797].

Interactive structures are available ([Jmol](#)).

Source : <http://www1.lsbu.ac.uk/water/hypec.html>