

Starch

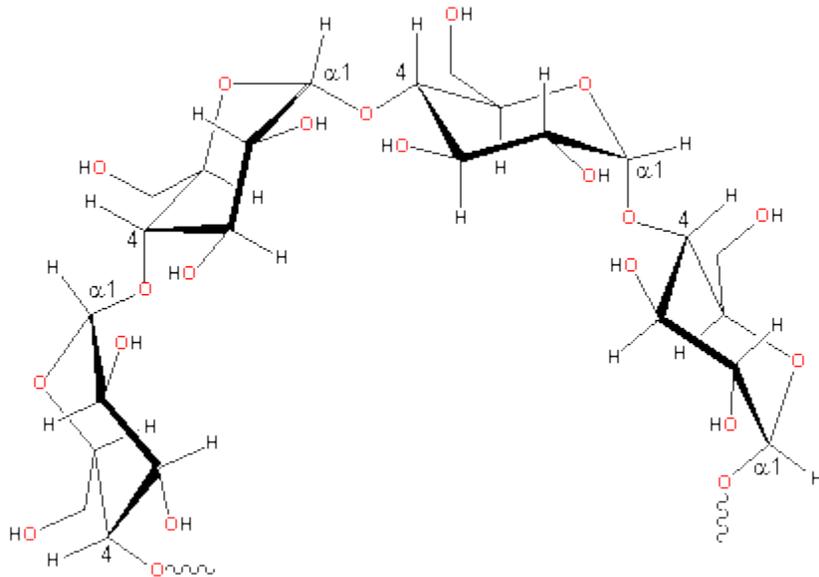
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Sources for starch

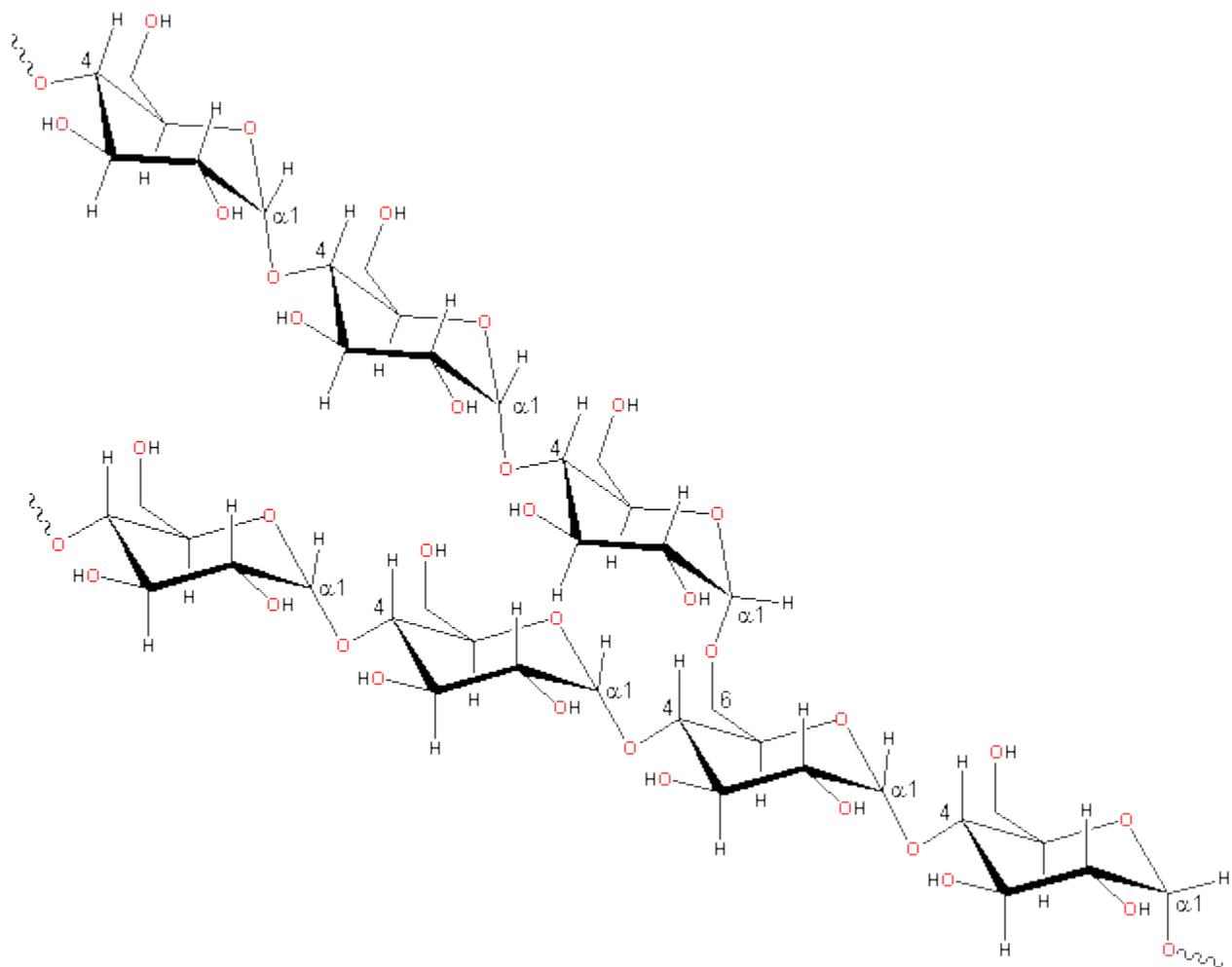
Starch is the major carbohydrate reserve in plant tubers and seed endosperm where it is found as granules [330, 1758] each typically containing several million amylopectin molecules accompanied by a much larger number of smaller amylose molecules. By far the largest source of starch is corn (maize) with other commonly used sources being wheat, potato, tapioca and rice. Amylopectin (without amylose) can be isolated from 'waxy' maize starch whereas amylose (without amylopectin) is best isolated after specifically hydrolyzing the amylopectin with pullulanase [405]. Genetic modification of starch crops has recently led to the development of starches with improved and targeted functionality [593].

Structural unit

Starch consists of two types of molecules, amylose (normally 20-30%) and amylopectin (normally 70-80%). Both consist of polymers of α -D-glucose units in the 4C_1 conformation. In amylose these are linked $-(1 \rightarrow 4)-$, with the ring oxygen atoms all on the same side, whereas in amylopectin about one residue in every twenty or so is also linked $-(1 \rightarrow 6)-$ forming branch-points. The relative proportions of amylose to amylopectin and $-(1 \rightarrow 6)-$ branch-points both depend on the source of the starch, for example, amylomaizes contain over 50% amylose whereas 'waxy' maize has almost none ($\sim 3\%$) [260].



Representative partial structure of amylose



Representative partial structure of amylopectin

Molecular structure

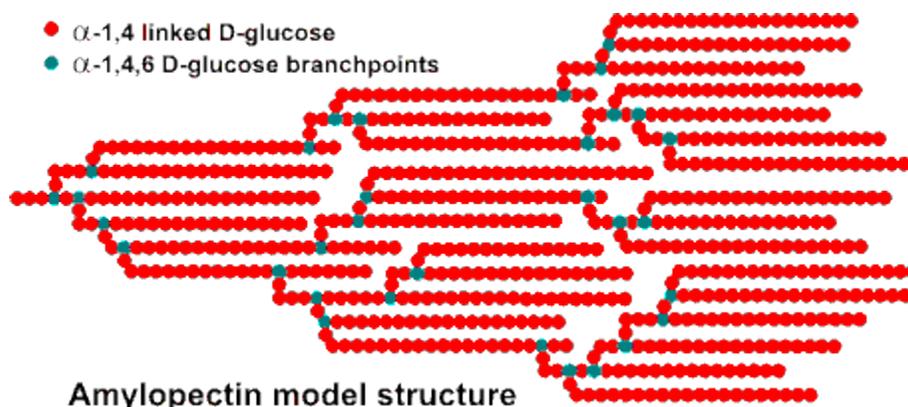
Amylose and amylopectin are inherently incompatible molecules; amylose having lower molecular weight with a relatively extended shape whereas amylopectin has huge but compact molecules. Determination of the molecular weight distribution of starch molecules presents several problems [1593]. The presence of amylose tends to reduce the crystallinity of the amylopectin and influence the ease of water penetration into the granules. Most of their structure consists of α -(1 \rightarrow 4)-D-glucose units. Although the α -(1 \rightarrow 4) links are capable of relatively free rotation around the (ϕ) *phi* and (ψ) *psi* torsions, hydrogen bonding between the O3' and O2 oxygen atoms of sequential residues tends to encourage a helical conformation. These helical structures are relatively stiff and may present contiguous hydrophobic surfaces.

Amylose

Amylose molecules consist of single mostly-unbranched chains with 500-20,000 α -(1 \rightarrow 4)-D-glucose units dependent on source (a very few α -1 \rightarrow 6 branches and linked phosphate groups may be found [258], but these have little influence on the molecule's behavior [330]). Amylose can form an extended shape (hydrodynamic radius 7-22 nm [263]) but generally tends to wind up into a rather stiff left-handed single helix or form even stiffer parallel left-handed double helical junction zones (Jmol, 39 KB, [339]). Single helical amylose has hydrogen-bonding O2 and O6 atoms on outside surface of the helix with only the ring oxygen pointing inwards. Hydrogen bonding between aligned chains causes retrogradation and releases some of the bound water (syneresis). The aligned chains may then form double stranded crystallites that are resistant to amylases. These possess extensive inter- and intra-strand hydrogen bonding, resulting in a fairly hydrophobic structure of low solubility. The amylose content of starches is thus the major cause of resistant starch formation (RS₃, see [below](#)).

Single helix amylose behaves similarly to the [cyclodextrins](#) by possessing a relatively hydrophobic inner surface that holds a spiral of water molecules, which are relatively easily lost to be replaced by hydrophobic lipid or aroma molecules. It is also responsible for the characteristic binding of amylose to chains of charged iodine molecules (for example, the polyiodides; chains of I₃⁻ and I₅⁻ forming structures such as I₉³⁻ and I₁₅³⁻; note that neutral I₂ molecules may give polyiodides in aqueous solution and there is no interaction with I₂ molecules except under strictly anhydrous conditions) where each turn of the helix holds about two iodine atoms and a blue color is produced due to donor-acceptor interaction between water and the electron deficient polyiodides.

Amylopectin

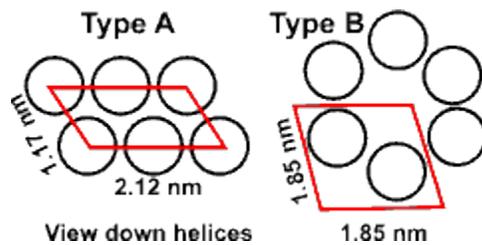
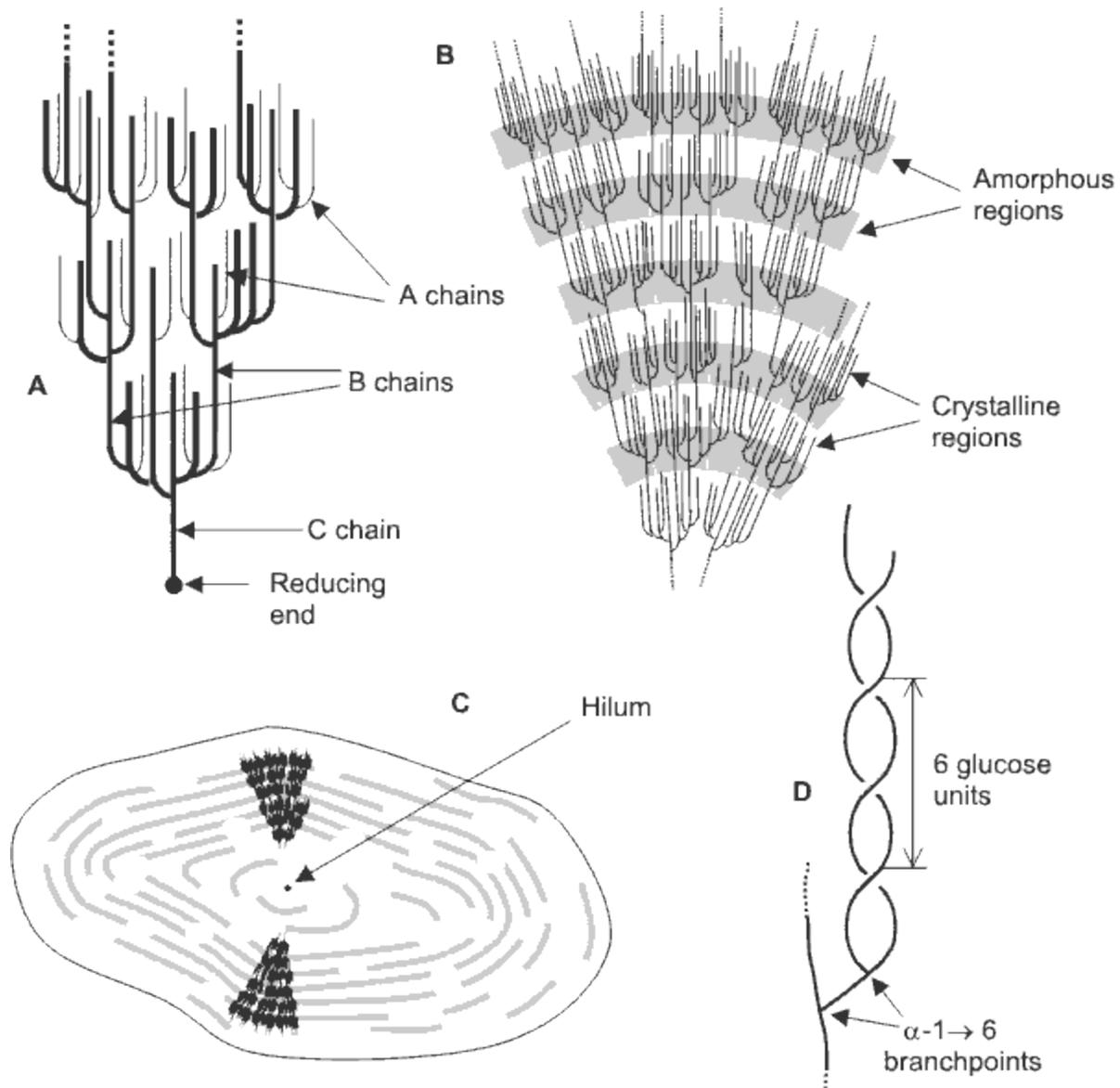


Amylopectin is formed by non-random α -1 \rightarrow 6 branching of the amylose-type α -(1 \rightarrow 4)-D-glucose structure. This branching is determined by branching enzymes that leave each chain with up to 30 glucose residues. Each amylopectin molecule contains a million or so residues, about 5% of which form the branch points. There are usually slightly more 'outer' unbranched chains (called A-chains)

than 'inner' branched chains (called B-chains). There is only one chain (called the C-chain) containing the single reducing group.

A-chains generally consist of between 13-23 residues [1479]. There are two main fractions of long and short internal B-chains with the longer chains (greater than about 23-35 residues) connecting between clusters and the shorter chains similar in length to the terminal A-chains [1479].

Each amylopectin molecule contains up to two million glucose residues in a compact structure with hydrodynamic radius 21-75 nm [263] (waxy maize amylopectin >300 nm [1683]). The molecules are oriented radially in the starch granule and as the radius increases so does the number of branches required to fill up the space, with the consequent formation of concentric regions of alternating amorphous and crystalline structure. In the diagram below: A - shows the essential features of amylopectin. B - shows the organization of the amorphous and crystalline regions (or domains) of the structure generating the concentric layers that contribute to the "growth rings" that are visible by light microscopy. C - shows the orientation of the amylopectin molecules in a cross section of an idealized entire granule. D - shows the likely double helix structure taken up by neighboring chains and giving rise to the extensive degree of crystallinity in granule. There is some debate over the form of the crystalline structure but it appears most likely that it consists of parallel left-handed helices with six residues per turn. An alternative arrangement of interconnecting clusters has been described for some amylopectins [1193].



Some amylopectin (for example, from potato) has phosphate groups attached to some hydroxyl groups, which increase its hydrophilicity and swelling power.^a Amylopectin double-helical chains can either form the more open hydrated Type **B** hexagonal crystallites or the denser Type **A** crystallites, with staggered monoclinic packing, dependent on the plant source of the granules [263]. Type **A**, with unbroken chain lengths of about 23-29 glucose units is found in most cereals.

Type **B**, with slightly longer unbroken chain lengths of about 30-44 glucose units is found in banana, some tubers such as potato and high amylose cereal starches. There is also a type **C** structure, which is a combination of types A and B and found in peas and beans. Starch granule architecture has been recently described [1008].

Functionality

Starch is a versatile and cheap, and has many uses as thickener, water binder, emulsion stabilizer and gelling agent. Its form and functionality have recently been reviewed [1556]. Starch is often used as an inherent natural ingredient but it is also added for its functionality. It is naturally found tightly and radially packed into dehydrated granules (about one water per glucose) with origin-specific shape and size (maize, 2-30 μm ; wheat, 1-45 μm ; potato, 5-100 μm [593]). The size distribution determines its swelling functionality with granules being generally either larger and lenticular (lens-like, **A**-starch) or smaller and spherical (**B**-starch) [1118] with less swelling power^a. Granules contain 'blocklets' of amylopectin containing both crystalline (~30%) and amorphous areas. As they absorb water, they swell, lose crystallinity and leach amylose. The higher the amylose content, the lower is the swelling power and the smaller is the gel strength for the same starch concentration. To a certain extent, however, a smaller swelling power due to high amylose content can be counteracted by a larger granule size [260]. Although the properties of starch are naturally inconsistent, being dependent on the vagaries of agriculture, there are several suppliers of consistently uniform starches as [functional ingredients](#).

Of the two components of starch, amylose has the most useful functions as a hydrocolloid. Its extended conformation causes the high viscosity of water-soluble starch and varies relatively little with temperature. The extended loosely helical chains possess a relatively hydrophobic inner surface that is not able to hold water well and more hydrophobic molecules such as lipids and aroma compounds can easily replace this. Amylose forms useful gels and films. Its association and crystallization (retrogradation) on cooling and storage decreases storage stability causing shrinkage and the release of water (syneresis). Increasing amylose concentration decreases gel stickiness but increases gel firmness. Retrogradation is affected by lipid content, amylose/amylopectin ratio, chain length of amylose and amylopectin, and solid concentration [1574]. Amylopectin interferes with the interaction between amylose chains (and retrogradation) and its solution can lead to an initial loss in viscosity and followed by a more slimy consistency. Mixing with [k-carrageenan](#), [alginate](#), [xanthan gum](#) and low molecular weight sugars can also reduce retrogradation. At high concentrations, starch gels are both [pseudoplastic](#) and [thixotropic](#) with greater storage stability. Their water binding ability (high but relatively weak) can provide body and texture to foodstuffs and is encouraging its use as a fat replacement.

A significant proportion of starch in the normal diet escapes degradation in the stomach and small intestine and is labeled 'resistant starch' (for recent reviews see [991]), but this portion is difficult to measure (see [1661] for methods) and depends on a number of factors including the form of starch and the method of cooking prior to consumption. Nevertheless resistant starch serves as a primary

source of substrate for colonic microflora, and may have several important physiological roles (see [hydrocolloids and health](#)). Resistant starch has been categorized as physically inaccessible (RS₁), (raw) ungelatinized starch (for example, in banana; RS₂^b), thermally stable retrograded starch (for example, as found in bread, especially stale bread, mainly amylose; RS₃) and chemically modified starch (RS₄). Resistant starch should be considered a dietary fiber. Although not exactly quantifiable due to its heterogeneous nature, some is determined by the official Association of Official Agricultural Chemists (AOAC) method. Starch with structure intermediate between the more crystalline resistant starch (for example, RS₃ in staled bread) and more amorphous rapidly digestible starch (for example, in boiled potato) is slowly digestible starch [293] (for example, in boiled millet). Slowly digestible starch gives reduced postprandial blood glucose peaks and is therefore useful in the diabetic diet.

Many functional derivatives of starch are marketed including cross-linked, oxidized, acetylated, hydroxypropylated and partially hydrolyzed material. For example, partially hydrolyzed (that is, about two bonds hydrolyzed out of eleven) starch (dextrin [1750]) is used in sauces to control viscosity.

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

Footnotes

^a Swelling power is determined after heating the starch in excess water and is the ratio of the wet weight of the (sedimented) gel formed to its dry weight. It will depend on the processing conditions (temperature, time, stirring, centrifugation) and may be thought of as its water binding capacity. [[Back](#)]

^b The amount of resistant starch is highest in unripe green bananas (~15%) and drops during ripening to much lower values as the starch is converted to glucose. [[Back](#)]

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