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Crystal Structure of a Maltogenic Amylase: Insights into a Catalytic Versatility

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Amylases catalyze the hydrolysis of starch material and play central roles in carbohydrate metabolism. The structure and a size exclusion column chromatography proved that the enzyme is a dimer in solution. The N-terminal segment of the enzyme folds into a distinct domain and comprises the enzyme active site together with the central ($\alpha/\beta)_8$ barrel of the adjacent subunit. Compared to many different amylases that are able to hydrolyze only α-D-(1,4)-glycosidic bonds, maltogenic amylases exhibit catalytic versatility; hydrolysis of α-D-(1,4)- and α-D-(1,6)-glycosidic bonds and transglycosylation of oligosaccharides to C3-, C4-, or C6- hydroxyl groups of various acceptor mono- or disaccharides.

It has been speculated that the catalytic property of the enzymes is linked to the additional 130 residues at the N-terminus that are absent in other typical α-amylases.

The crystal structure of a maltogenic amylase from a thermus strain was determined at 2.8 A. The active site is a narrow and deep cleft suitable for binding cyclodextrins, which are the preferred substrates to other starch materials. At the bottom of the active site cleft, an extra space, absent in the other typical α-amylases, is present whose size is comparable to that of a dissaccharide. The space is most likely to host an acceptor molecule for the transglycosylation and to allow binding of a branched oligosaccharide for hydrolysis of α-D-(1,4)-glycosidic or α-D-(1,6)-glycosidic bond. The ($\alpha/\beta)_8$ barrel of the enzyme is the preserved scaffold in all the known amylases. The structure represents a novel example of how an enzyme acquires a different substrate profile and a catalytic versatility from a common active site, and represents a framework for explaining the catalytic activities of transglycosylation and hydrolysis of α-D-(1,6)-glycosidic bond.