Two carbohydrate binding surface sites (SBSs) on barley α-amylase 1 (AMY1) of glycoside hydrolase family 13 (GH13) displayed synergy in interactions with starch granules, thus being pivotal for hydrolysis of supramolecular substrates. Mutational analysis showed that SBS1 is more critical for the conversion of starch granules, while SBS2 has higher affinity than SBS1 for β-cyclodextrin (β-CD). Noticeably, the binding preference of β-CD to SBS2 differed distinctly from that of maltotriose to the catalytic nucleophile mutant D180A AMY1. Binding energy maps at subsites -4 through +4 of the active site indicated remarkably elevated affinity due to the Y380A mutation at SBS1. The high-yield AMY2 expression variant A42P, made it possible to show that Tyr378—corresponding to Tyr380 in AMY1—has a role in interactions with starch granules, but not in β-CD binding. Besides SBSs, dedicated starch binding domains (SBDs) mediate binding to starch granules. SBDs are currently categorised into 9 carbohydrate binding module (CBM) families. A novel CBM20 subfamily encountered in regulatory enzymes possesses characteristically low affinity for β-CD. Although α-amylase is essential for starch mobilisation in germinating barley seeds, efficient degradation requires the concerted action of α-amylase, β-amylase, limit dextrinase (LD) and possibly α-glucosidase. Limit dextrinase (LD) is encoded by a single gene and represents the sole debranching activity during germination. Recent expression of functional LD in Pichia pastoris makes biochemical and biophysical characterisation of this GH13 enzyme possible. An endogenous limit dextrinase inhibitor was cloned and produced recombinantly and demonstrated to have sub-nanomolar affinity for LD.