α-Glucan debranching enzymes hydrolyse α-1,6-linkages in starch/glycogen, thereby, playing a central role in energy metabolism in all living organisms. They belong to glycoside hydrolase families GH13 and GH57 and several of these enzymes are industrially important. Nine GH13 subfamilies include α-glucan debranching enzymes; isoamylase and glycogen debranching enzymes (GH13_11); pullulanase type I/limit dextrinase (GH13_12–14); pullulan hydrolase (GH13_20); bifunctional glycogen debranching enzyme (GH13_25); oligo-1 and glucan-1,6-α-glucosidases (GH13_31); pullulanase type II (GH13_39); and α-amylase domains (GH13_41) in two-domain amylase-pullulanases. GH57 harbours type II pullulanases. Specificity differences, domain organisation, carbohydrate binding modules, sequence motifs, three-dimensional structures and specificity determinants are discussed. The phylogenetic analysis indicated that GH13_39 enzymes could represent a “missing link” between the strictly α-1,6-specific debranching enzymes and the enzymes with dual specificity and α-1,4-linkage preference.