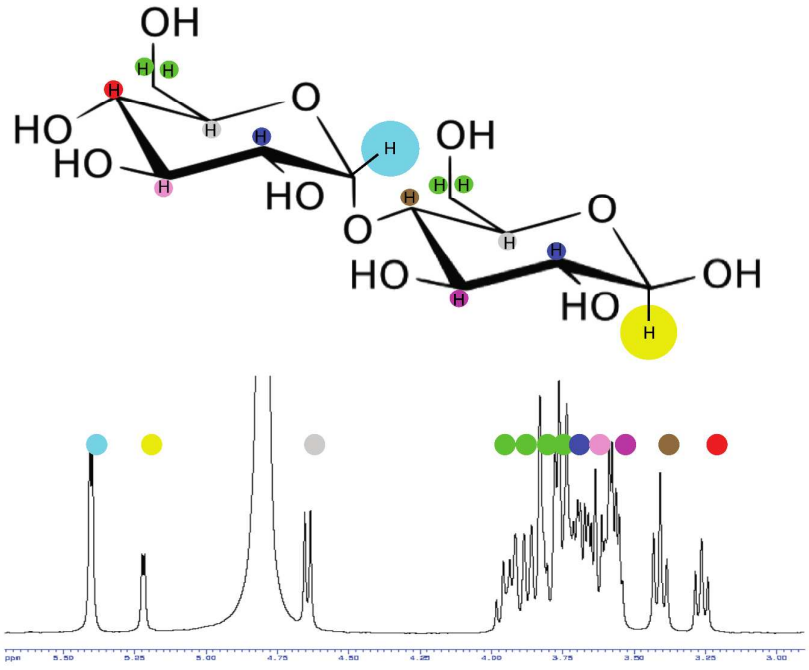
Supporting Information (SI)



SI Figure S1. The assignment of protons from maltose. The colored protons correspond to the proton resonances in the spectrum shown. The resonances from the C1 protons (light blue, yellow) both fall in the region 5-6 ppm. The resonance from the reducing C1 proton (yellow) is not observed in the spectrum of starch (Figure 1b i, main article).

SI Figure S2. Optical microscopy video of starch granule swelling. Starch granules were heated from 20° to 100°C at a rate of 2° per minute and viewed microscopically under crossed polarised light. The starch granules swell in a temperature range of 65° to 75°C.

SI Table S1 Michaelis-Menten Parameters for amylolysis at 37^{O}C of hydrothermally pre-treated granules. Values in Table represent the mean ± standard error of triplicate experiments. The fraction susceptible to amylolysis was calculated using $K_M^{amy} / K_M^{\exp}$ x 100.

Pre-treatment temperature °C	k_{cat} **min^{-1}**	$K_M^{\exp}$ **mg.ml^{-1}**	**Susceptible fraction (%)**
25	6600 ± 460	12.00 ± 0.10	6.1 ± 0.5
60	17700 ± 1200	13.40 ± 1.3	5.5 ± 0.5
65	11000 ± 300	2.11 ± 0.05	34.6 ± 0.8
70	14000 ± 100	0.96 ± 0.07	76.4 ± 5.8
80	13700 ± 170	0.81 ± 0.02	90.3 ± 2.3
90	13800 ± 800	0.86 ± 0.28	84.6 ± 27
100	14600 ± 580	0.77 ± 0.22	94.6 ± 26