

Article

Unambiguous *ex situ* and *in cell* 2D ^{13}C solid-state NMR characterization of starch and its constituents

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Table S1. Crystallinity evaluation using the method suggested by Lopez *et al.* (2008) ¹ on 1D CP NMR experiments for extracted and *in situ* starch from wild-type (*wt*), amylopectin-rich starch (*ap*), amylose-rich starch (*as*), native retrograded (*retro*) and dry amorphous amylose (*am*).

Figure S1. XRD diffractograms of dry (left column) and hydrated (right column) samples. XRD diffractograms are acquired on amylopectin-rich (A-type) (**A**), native retrograded (B-type) (**B**), amylose-rich (C), native *C. reinhardtii* (**D**) and amorphous (**E**) starches.

Figure S2. Overlapped CP-INADEQUATE of pure *C. reinhardtii* native starch (**black**) and amorphous dry amylose (**red**). Dashed lines represent spin system of amorphous starch determined using CP-INADEQUATE on native *C. reinhardtii* starch. Here CP is used instead of NOE-INADEQUATE because the polarization transfer lead to a better resolution in the amorphous region.

Figure S3. 1D cross-polarisation ¹³C solid-state NMR spectra of amylopectin (**A**) and amylose (**B**) starches from *C. reinhardtii* strains *st 2-1* and *sta 3-3*, respectively.

Figure S4. Overlapped NOE-INADEQUATE of pure *C. reinhardtii* amylopectin-rich starch (**black**) and amylose-rich starch (**red**). Dashed lines represent spin system of B-type starch while continuous lines are A-type starch. Here, amylose starch is not crystalline enough to make a clear difference with the highly crystalline amylopectin-rich starch.

Figure S5. Overlapped NOE-INADEQUATE of pure *C. reinhardtii* native (**red**) and amylopectin-rich (**black**) starches.

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		wt	ap	as	retro	am
NMR	<i>extracted</i>	62.9	71.2	38.0	54.5	0.1
	<i>in situ</i>	62.3	69.9	40.0		

¹ Lopez-Rubio, A.; Flanagan, B. M.; Gilbert, E. P.; Gidley, M. J. A novel approach for calculating starch crystallinity and its correlation with double helix content: a combined XRD and NMR study. *Biopolymers* **2008**, 89, (9), 761-8.

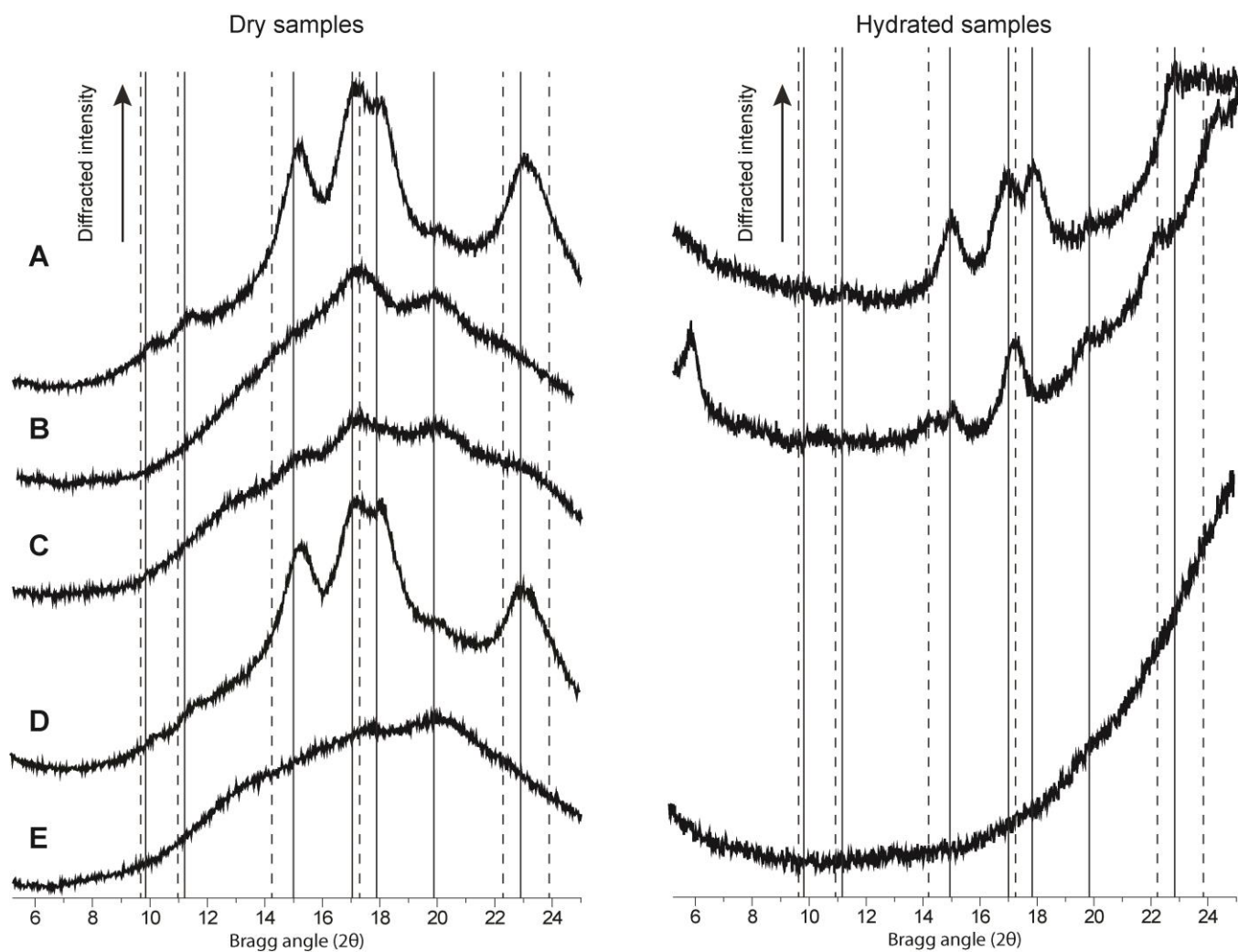


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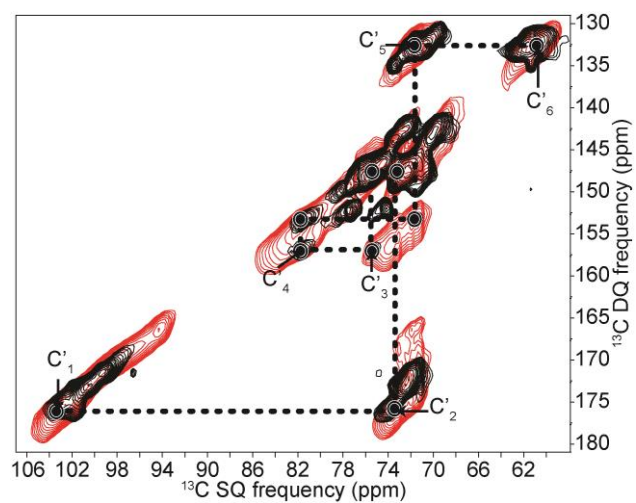


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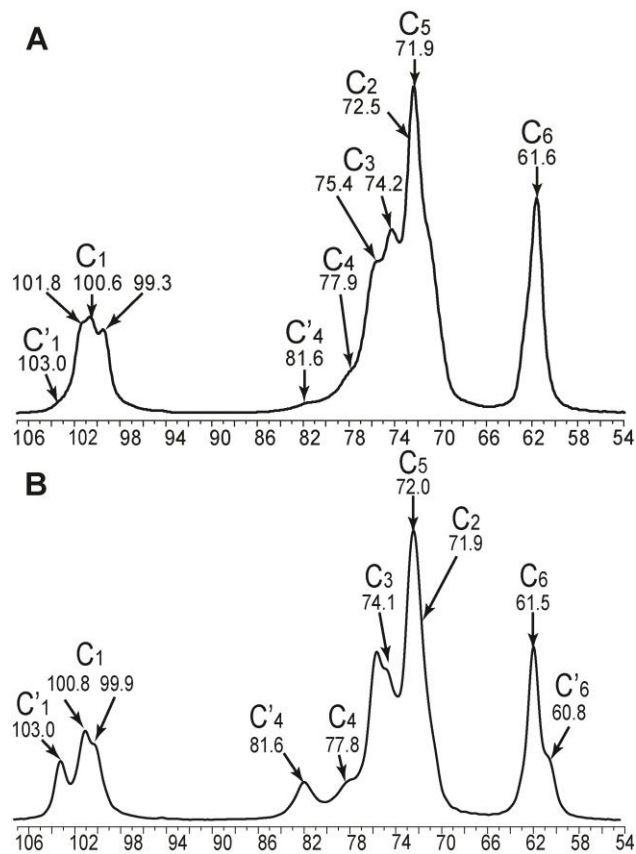


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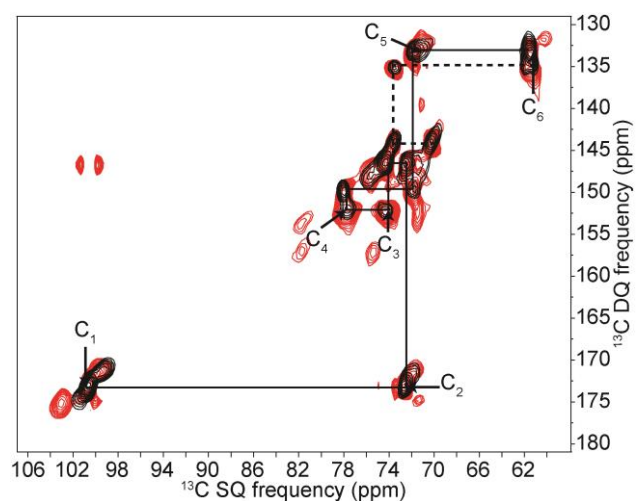


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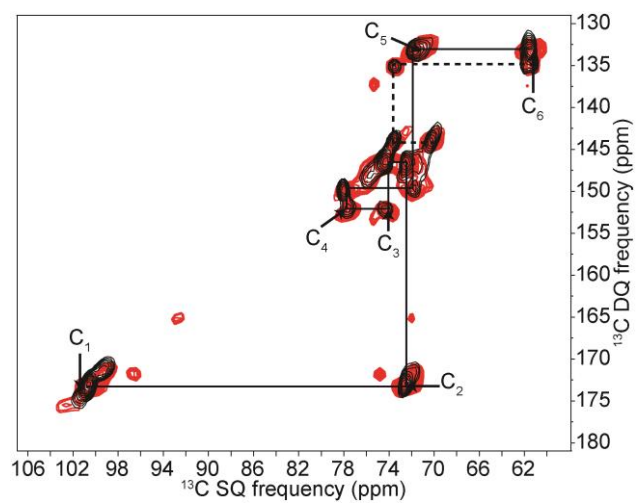


Figure S5. Overlapped ^{13}C NOE-INADEQUATE of pure *C. reinhardtii* native (**red**) and amylopectin-rich (**black**) starches.