

**Supplemental data**  
**to**  
**IsoMalto/Malto-Polysaccharide, A Novel Soluble Dietary Fibre Made Via**  
**Enzymatic Conversion of Starch**

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**Table S1.** The degree of branching of eight starches.

The degree of branching has been determined by measuring the increase in reducing ends upon debranching with isoamylase. All values have been determined in the same experiment. The values are plotted versus the percentage of ( $\alpha$ 1 $\rightarrow$ 6)-glycosidic linkages in the IMMPs derived of the starches (Fig. 2b of the main text). IMMPs are linear ( $\alpha$ 1 $\rightarrow$ 6)-glucan chains attached to the non-reducing ends of starch fragments, *i.e.* ( $\alpha$ 1 $\rightarrow$ 4)-glucan chains. Reducing ends were quantified using the Nelson- Somogyi method (1,2).

Starch	Degree of branching ( $\alpha$ 1 $\rightarrow$ 4,6) (%) <sup>a</sup>
Corn	3.61
Potato	3.09
Rice	4.06
Tapioca	3.93
Waxy corn	4.81
Waxy potato	3.97
Waxy rice	4.93
Wheat	3.70

<sup>a</sup> To be published elsewhere.

**Table S2.** The dietary fibre content of IMMPs derived of indicated substrates.

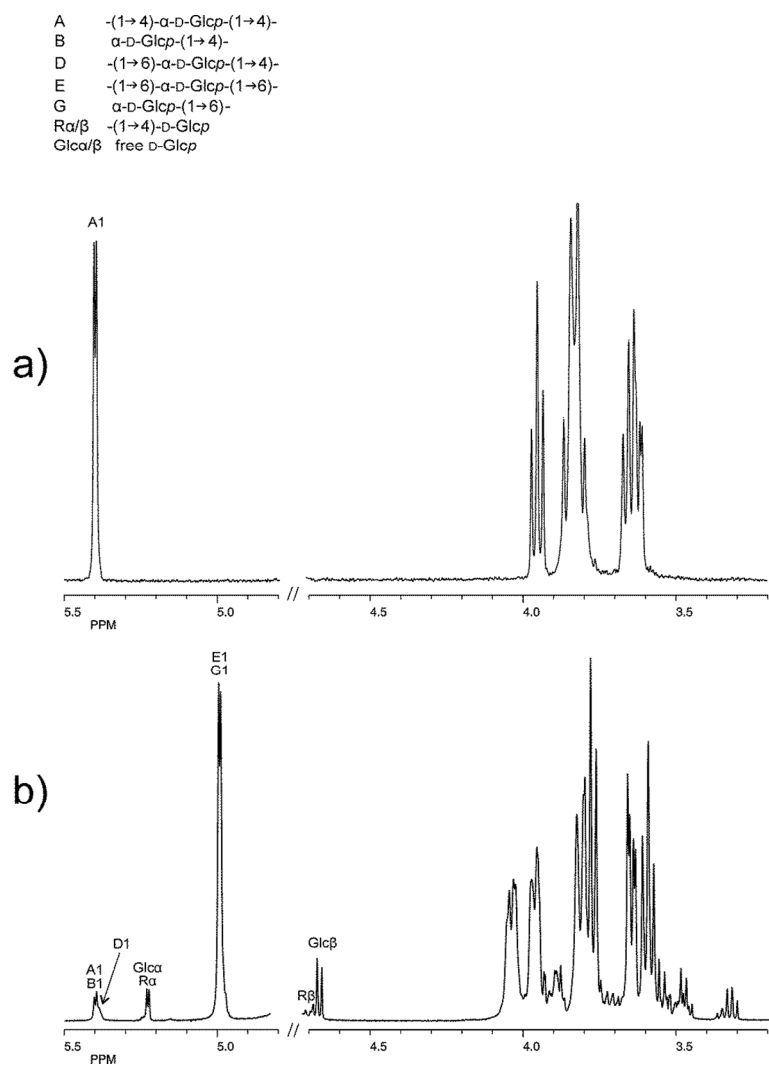
Substrate	GTFB treated	Debranched	% ( $\alpha$ 1 $\rightarrow$ 6) in product	HMWDF <sup>a</sup> (%)	LMWDF <sup>b</sup> (%)	TDF <sup>c</sup> (%)
Paselli MD10	-	-	4	0.4	0.3	0.7
Paselli MD10	+	-	33	19.4	5.7	25.1
Paselli MD6	-	-	4	0.5	1.1	1.6
Paselli MD6	+	-	34	19.8	7.2	27.0
Paselli SA2	-	-	4	0.7	0.3	1.0
Paselli SA2	+	-	32	17.1	2.9	20.0
Eliane MD6	-	-	4	0.4	3.3	3.7
Eliane MD6 <sup>d</sup>	+	isoamylase	50	30.5	8.5	39.0
Eliane MD6 <sup>d</sup>	+	isoamylase	61	36.0	8.8	44.8
Waxy potato	+	isoamylase	83	56.4	4.3	60.7
Potato starch	+	pullulanase	92	85.7	1.3	87.1

<sup>a</sup> HMWDF, high-molecular-weight dietary fibre.

<sup>b</sup> LMWDF, low-molecular-weight dietary fibre.

<sup>c</sup> TDF, total dietary fibre.

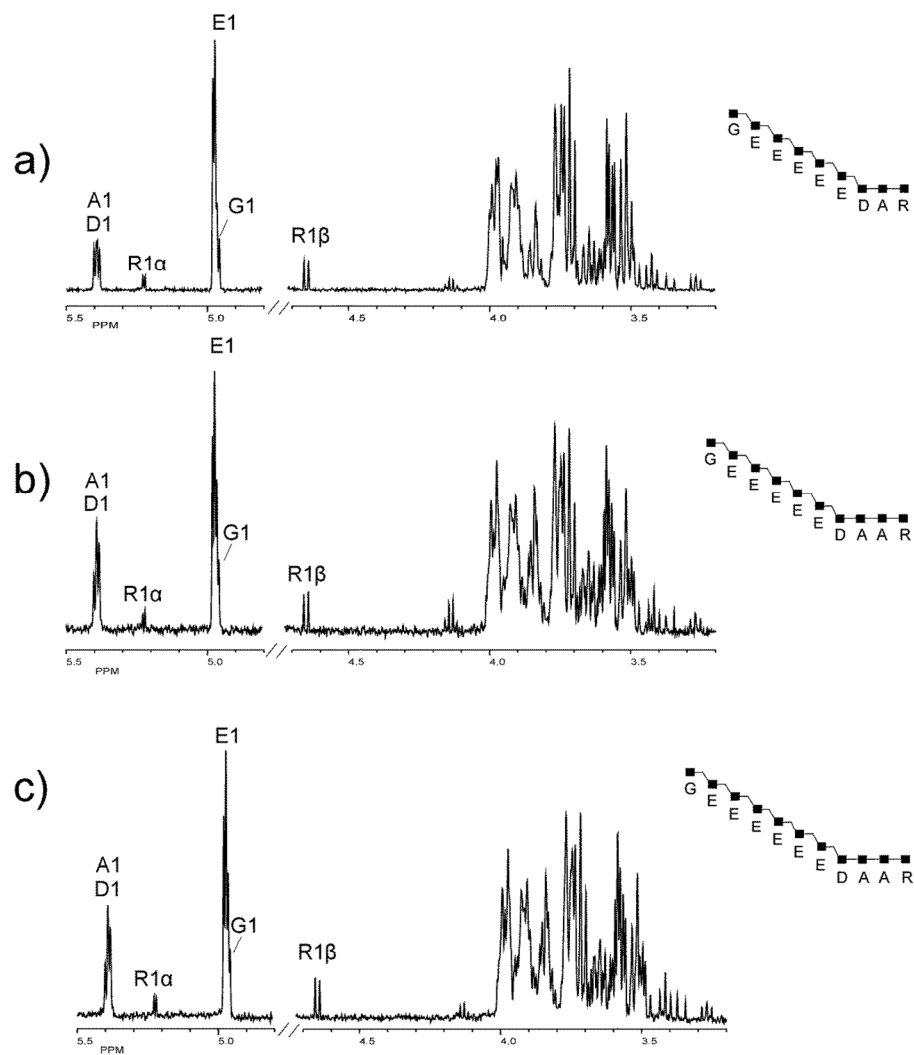
<sup>d</sup> Different reaction times were used, resulting in IMMPs with different amounts of ( $\alpha$ 1 $\rightarrow$ 6) linkages, because reactions were not yet completed.



**Fig. S1.** 1D  $^1\text{H}$ -NMR spectra ( $\text{D}_2\text{O}$ , 300K) of (a) amylose V and (b) the IMMP product derived of amylose V upon incubation with GTFB.

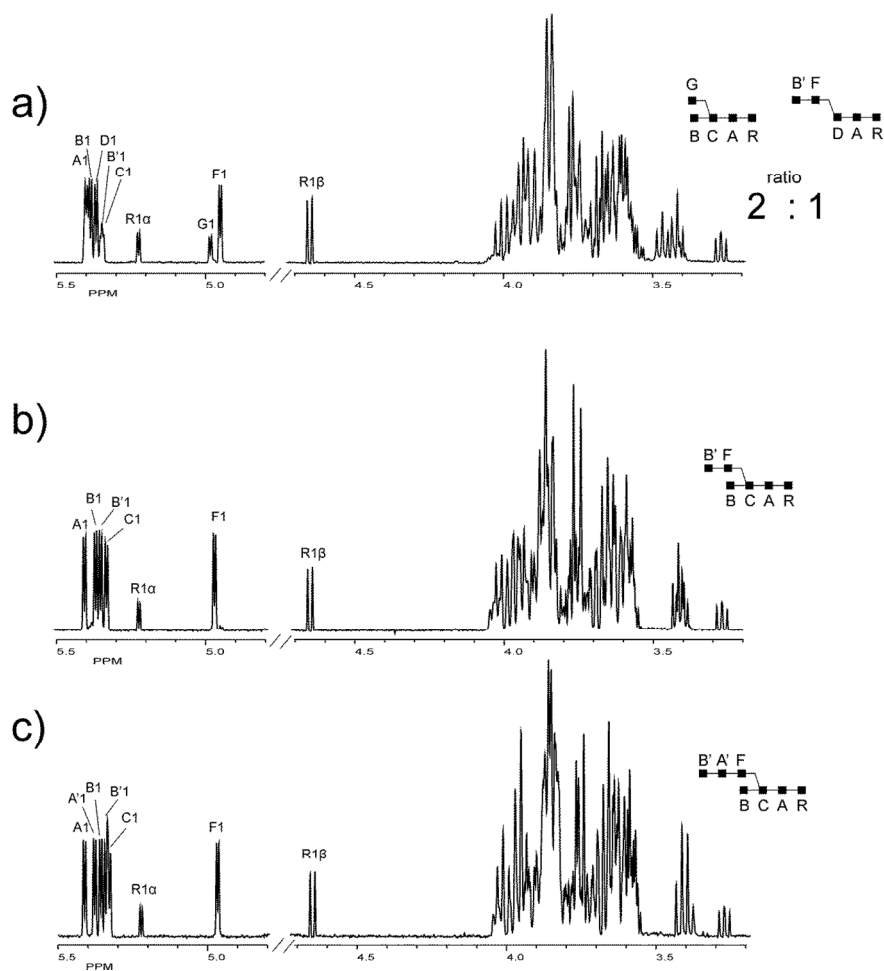
A  $-(1\rightarrow4)-\alpha\text{-D-Glcp}-(1\rightarrow4)-$   
 D  $-(1\rightarrow6)-\alpha\text{-D-Glcp}-(1\rightarrow4)-$   
 E  $-(1\rightarrow6)-\alpha\text{-D-Glcp}-(1\rightarrow6)-$   
 G  $\alpha\text{-D-Glcp}-(1\rightarrow6)-$   
 R $\alpha/\beta$   $-(1\rightarrow4)\text{-D-Glcp}$

■ :  $\alpha\text{-D-Glcp}$   
 ~ : 1 $\rightarrow$ 6 bond  
 - : 1 $\rightarrow$ 4 bond

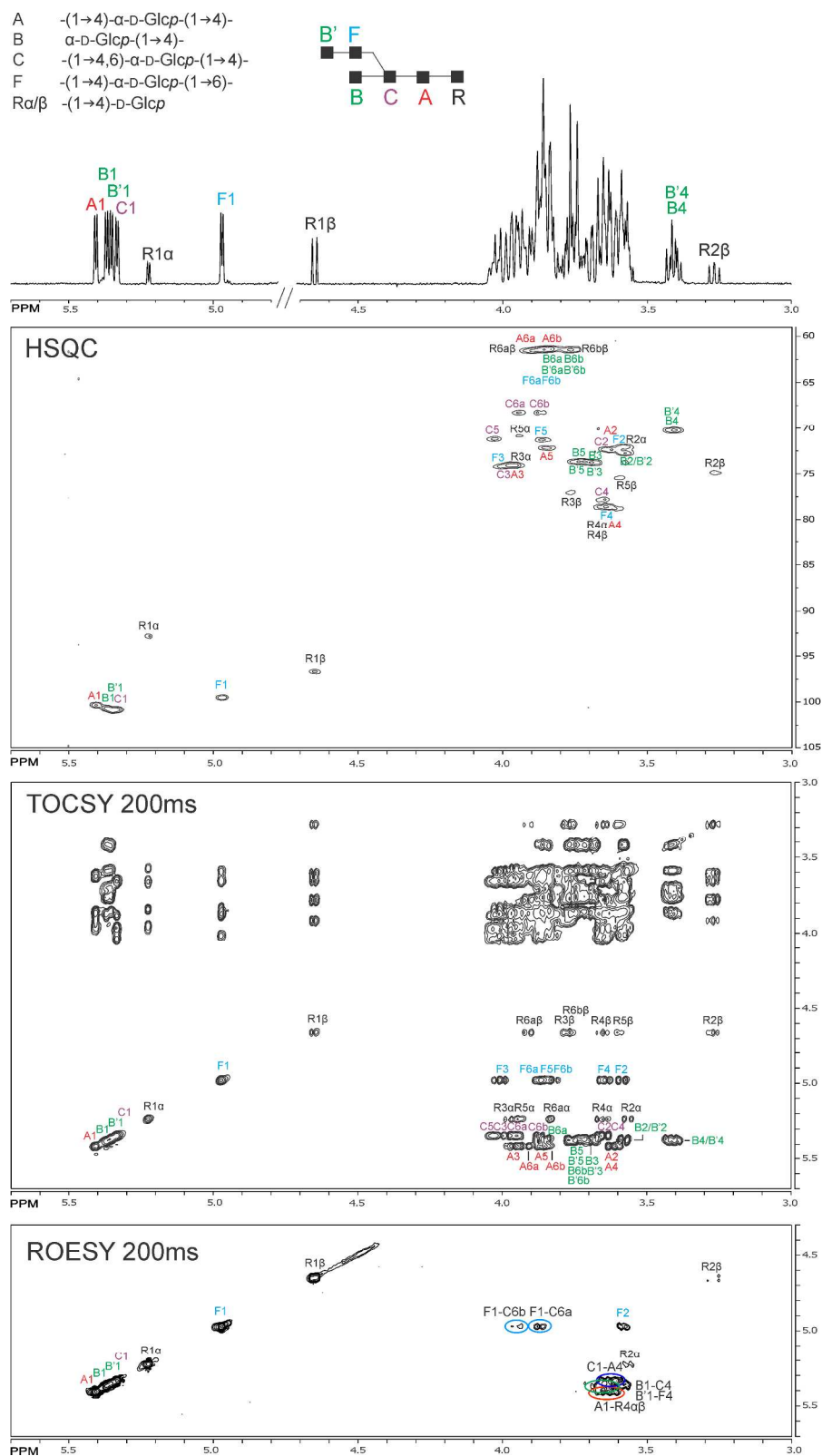


**Fig. S2.** 1D  $^1\text{H}$ -NMR spectra ( $\text{D}_2\text{O}$ , 300K) of linear oligosaccharides 11 (a), 15 (b) and 16 (c) from Fig. 4 of the main text. These compounds were purified from the  $\alpha$ -amylase treated IMMP derived of Paselli MD10.

- A  $-(1\rightarrow4)-\alpha\text{-D-Glcp}-(1\rightarrow4)-$   
 B  $\alpha\text{-D-Glcp}-(1\rightarrow4)-$   
 C  $-(1\rightarrow4,6)-\alpha\text{-D-Glcp}-(1\rightarrow4)-$   
 D  $-(1\rightarrow6)-\alpha\text{-D-Glcp}-(1\rightarrow4)-$   
 F  $-(1\rightarrow4)-\alpha\text{-D-Glcp}-(1\rightarrow6)-$   
 G  $\alpha\text{-D-Glcp}-(1\rightarrow6)-$   
 R $\alpha/\beta$   $-(1\rightarrow4)\text{-D-Glcp}$
- :  $\alpha\text{-D-Glcp}$   
 \(\curvearrowleft\) : 1 $\rightarrow$ 6 bond  
 - : 1 $\rightarrow$ 4 bond



**Fig. S3.** 1D  $^1\text{H-NMR}$  spectra ( $\text{D}_2\text{O}$ , 300K) of branched oligosaccharides 21 (a), 22 (b) and 23 (c) from Fig. 4 of the main text. Note that compound 21 was purified as a mixture together with compound 20. These compounds were purified from the  $\alpha$ -amylase treated IMMP derived of Paselli MD10.



**Fig. S4.** 1D/2D  $^1\text{H}$ -NMR spectra of compound 22 (Fig. 4 of main text) recorded in  $\text{D}_2\text{O}$  at 300K. Compound 22 was purified from the  $\alpha$ -amylase treated IMMP derived of Paselli MD10.

The 1D  $^1\text{H}$ -NMR spectrum of compound 22 showed seven anomeric signals, which were used as starting points for the assignment of the chemical shifts of all protons in the 2D TOCSY spectrum (TOCSY spectra with spin-lock times 20, 50, 100, and 200 ms were used to acquire all assignments). The H-1 signals at  $\delta$  5.223 (**R1** $\alpha$ ) and 4.650 (**R1** $\beta$ ) are in agreement with a reducing  $-(1\rightarrow4)\text{-D-Glcp}$  **R** unit (3,4). The anomeric signals at  $\delta$  5.406 (**A**),  $\delta$  5.332 (**C**) and 4.970 (**F**) reflect the presence of an internal  $-(1\rightarrow4)\text{-}\alpha\text{-D-Glcp-(1}\rightarrow4)\text{-}$  unit, a branched  $-(1\rightarrow4,6)\text{-}\alpha\text{-D-Glcp-(1}\rightarrow4)\text{-}$  unit and a  $-(1\rightarrow4)\text{-}\alpha\text{-D-Glcp-(1}\rightarrow6)\text{-}$  unit, respectively (4,5). Residue **B** ( $\delta$  5.369) showed a proton pattern similar to **B'** ( $\delta$  5.352), in the same track, indicating the presence of two terminal  $\alpha\text{-D-Glcp-(1}\rightarrow4)\text{-}$  units. In the 2D ROESY spectrum, strong inter-residual couplings were observed between **A** H-1 and **R** $\alpha$  H-4, **A** H-1 and **R** $\beta$  H-4, **C** H-1 and **A** H-4, **B** H-1 and **C** H-4, **F** H-1 and **C** H-6a/b, and **B'** H-1 and **F** H-4, in accordance with the structure  $\alpha\text{-D-Glcp-(1}\rightarrow4)\text{-}\alpha\text{-D-Glcp-(1}\rightarrow6)\text{-}[\alpha\text{-D-Glcp-(1}\rightarrow4)\text{-}]\alpha\text{-D-Glcp-(1}\rightarrow4)\text{-}\alpha\text{-D-Glcp-(1}\rightarrow4)\text{-D-Glcp}$ . The various substitution patterns are confirmed by their  $^{13}\text{C}$  NMR data, deduced from the  $^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum: **R** $\alpha$  (C-4,  $\delta$  78.5), **R** $\beta$  (C-4,  $\delta$  78.5), **A** (C-4,  $\delta$  78.5), **C** (C-4,  $\delta$  77.7; C-6  $\delta$  68.1) and **F** (C-4,  $\delta$  78.5) (5,6).

## References

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