NEO-AMYLOPECTINYL MODELS SYNTHESIS OF COMPLEX BETA-BRANCHED MALTO-OLIGOSACCHARIDES IN SOLUBLE AND SOLID PHASE

Christophe Bliard, Virginie Glaçon

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SYNTHESIS OF COMPLEX BETA-BRANCHED MALTO-OLIGOSACCHARIDES IN SOLUBLE AND SOLID PHASE.

Christophe BLIARD & Virginie GLAÇON

FRE 2715 CNRS, UFR Sciences, bâtiment 18 Europol'Agro, Moulin de la Housse, BP 1039, 51687 Reims cedex 2

Tel: 03 26 91 34 95 / Fax : 03 26 91 35 96 / christophe.bliard@univ-reims.fr

Abstract:

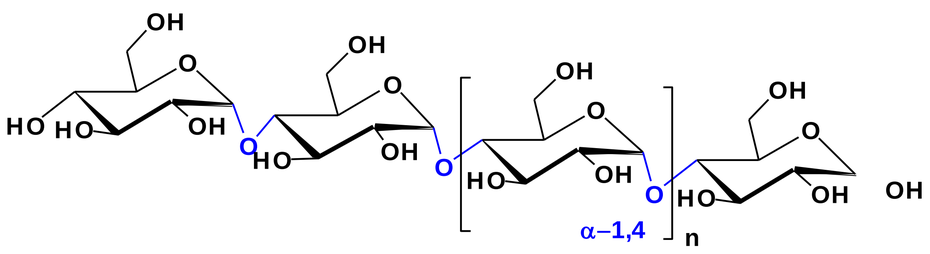
Starch is the ubiquitous glucidic reserve compound in nature. Synthesized by most plants from solar energy it is easily produced in very large scale cultures (cereals, tubers, legumes…). Besides its irreplaceable position in the food chain Starch is also a widely used commodity for its non-alimentary properties (paper, textile industry, adhesive, gels…) in almost all human activities[1]. Though the polysaccharidic nature and the basic structure : polya(1-4) glucopyrannose of its minor constituent Amylose, and α(1-6) branched α(1-4) polyglucopyrannose of the major amylopectin has long been known, to date, the fine primary structure of the former still remains to be described ! The branching pattern found in amylopectin can reach extreme complexity. The determination of amylopectins' primary structures from various botanical origins families can be a real challenge. Moreover, though the enzymes involved in starch synthesis have been well-described[2], no satisfactory in-vitro synthesis has been achieved to date, one of the reasons invoked being the lack of proper primer substrate[3]. In this paper we present an investigation of such structural diversity by re-building well-defined branched malto-oligosaccharidic model structures through chemical hemisynthesis, in order to obtain such substrates. Several isoamylase resistant, beta-branched neo-amylopectinyl oligosaccharides having degrees of polymerisation (DP) 4 to 8, with well-defined structures, were obtained. The construction of these models was performed using chemically modified malto-oligosaccharides in solution. All structures were confirmed by long distance heteronuclear NMR spectroscopy. Using activated Wang resin, solid-phase supported oligosaccharides were synthesised and the structures analysed by HR-MAS NMR.

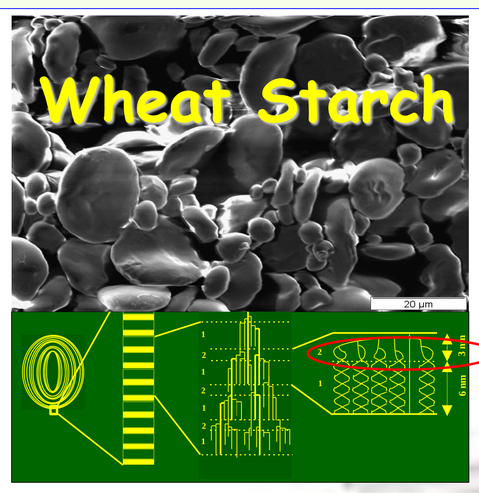
1- Sicard P.J. L'actualité chimique 11-12 (2002) 23-26

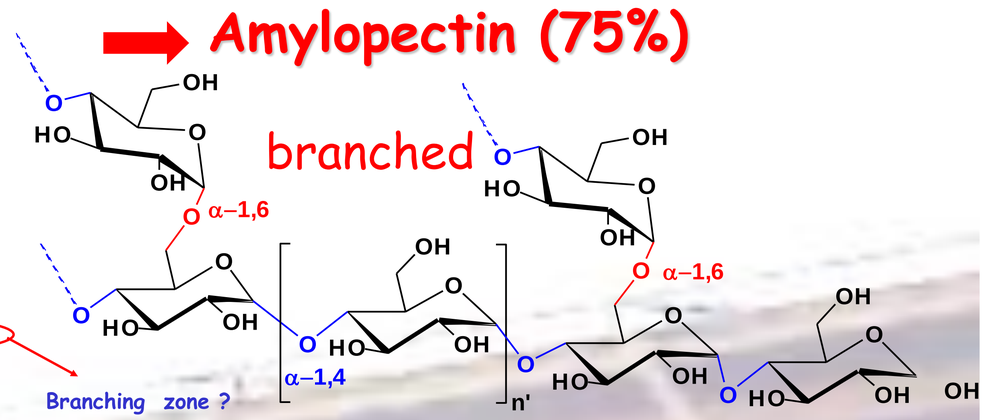
2 - Buléon A., Colonna P., Planchot V., Ball S., Int. J. Biol. Macromolecules, 23, (1998) 85-112.

3 - Ball S. et al., Cell, 86(1996)349-352

Amylose (25%) ← **Wheat Starch** → **Amylopectin (75%)**



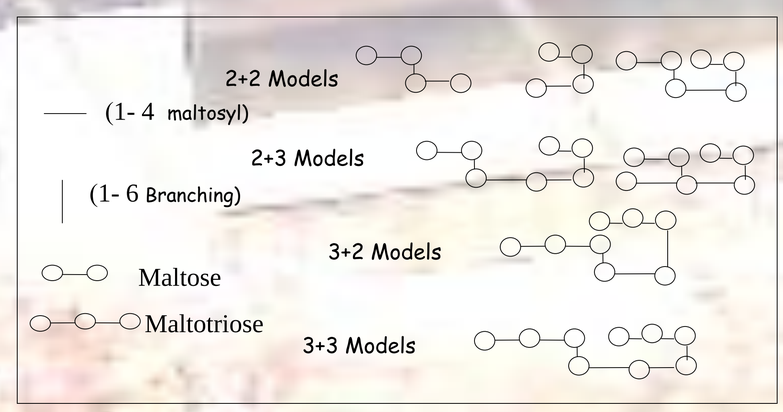




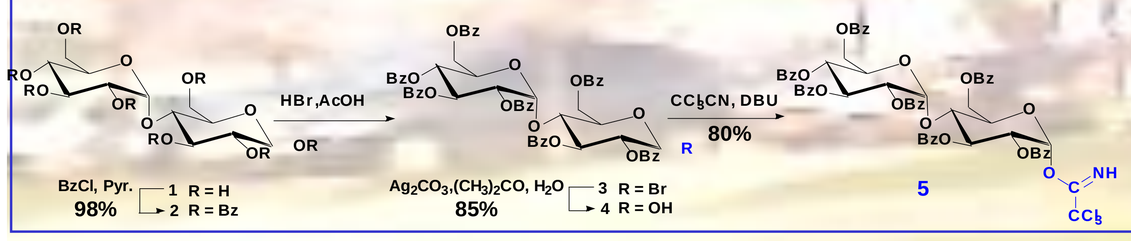
Oligosaccharide Syntheses :

The model oligosaccharides, chosen as targets were the neo-amylopectines β–branched analogs. Retro-synthesis analysis showed the possibility a fast, flexible and easy access of a large variety of well defined specific branched structures of DP 3 to 9 from maltose and maltotriose in 7 to 11 steps. Oligosaccharides up to DP 8 branched neo-amylopectinyl models were synthesized from common activated substrates on selectively protected di- and trisaccharide derivatives. These derivatives are destined :

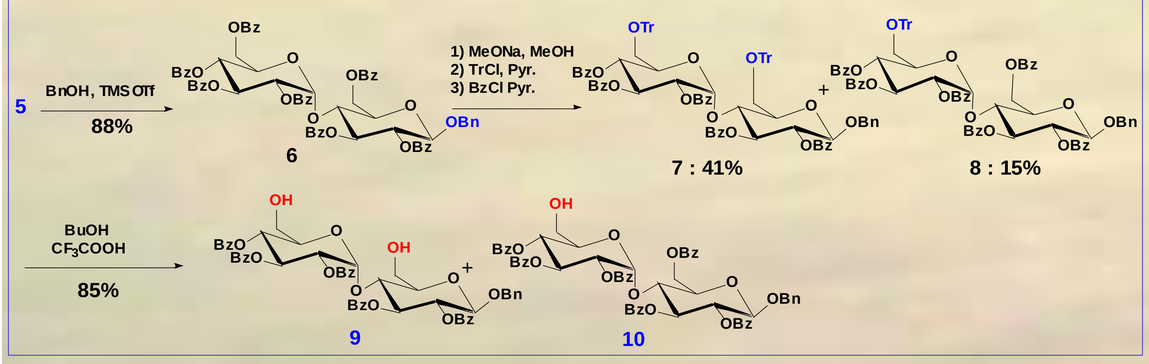
- to enzymatic test on starch synthetases and hydrolases in order to study biosynthesis and biodegradation
- to serve as RMN structure references in the analysis of limit dextrines from amylopectine enzymatic degradation
- to serve as reference in stuctural analysis (influence of parameters such as inter-branched chain distances).



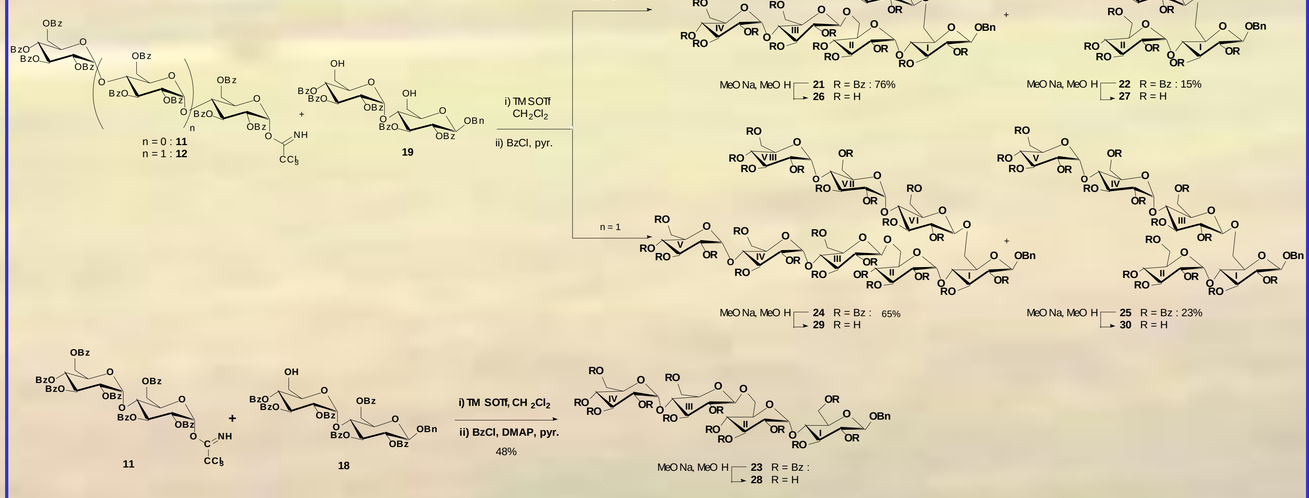
✓ Synthesis of activated maltosyl derivative 5



✓ Synthesis of maltosyl acceptors 9 et 10

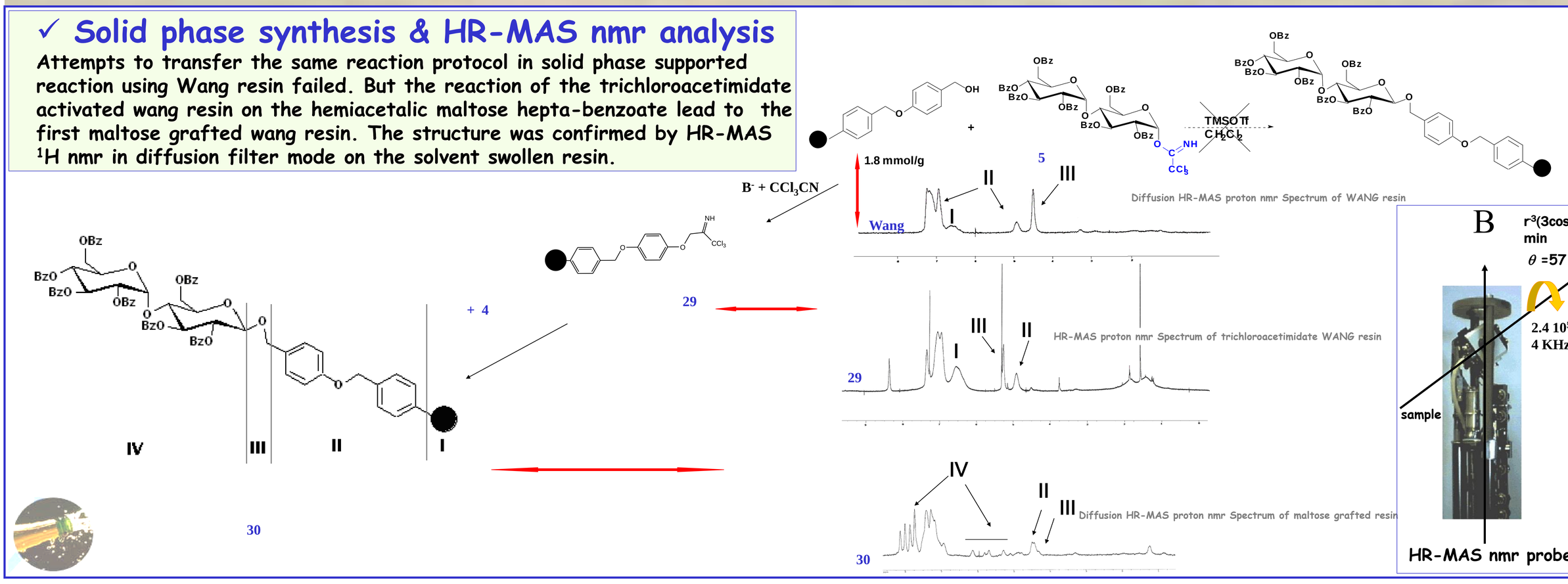


✓Synthesis of tera- penta, hexa and octasaccharides branched models 21, 22, 23, 24



✓ Solid phase synthesis & HR-MAS nmr analysis

Attempts to transfer the same reaction protocol in solid phase supported reaction using Wang resin failed. But the reaction of the trichloroacetimidate activated wang resin on the hemiacetalic maltose hepta-benzoate lead to the first maltose grafted wang resin. The structure was confirmed by HR-MAS ^{1}H nmr in diffusion filter mode on the solvent swollen resin.



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