



In the depth of oligosaccharidic structural complexity The example of multiply branched glycans

C. Bliard

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In the depth of oligosaccharidic structural complexity The example of multiply branched glycans

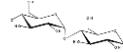
C. Bliard

Abstract:

Random cleavage of branched reserve polysaccharides composed of two different (malto-, m) and (isomalto-, i) linking types lead to complex oligomeric mixtures of various polymeric degree (DP). Each DP is a mixture of molecules containing potentially all combinations of (m) and/or (i) sub-structures. Industrial hydrolysis of starches polysaccharides produce syrups with a low DP (typically from 1 to 20). The number of potential oligosaccharidic structures accessible by random hydrolysis grow exponentially with the DP. The number of isomeric structures for each given DP (n) is a Catalan number, noted $C(n)$, calculated as $(2n \text{ choose } n)/(n+1) = (2n)!/(n!(n+1)!)$. The calculation gives 2 isomers (maltose and isomaltose) for (DP2), 16796 deca-saccharides potential isomers (DP10) and more than 6 billions eicosasaccharide isomers (DP20).

Introduction:

Glucose storage polysaccharides amylopectin or glycogen are huge polysaccharides composed of α -1,4 linked (malto-, m) chains branched on each other in a cascade of α -1,6 (isomaltosyl-, i) Chains with molecular sizes of 80 kDa up to several millions. Enzymatic or acid endolysis liberates malto-isomaltosyl oligosaccharides (MIMOS) of various degrees of polymerisation (DP). Unlike oligosaccharides obtained by degrading linear polysaccharides each DP fraction contains a multiplicity of Variously branched structure



In the course of a collaborative research program devoted to separating and purifying malto-oligosaccharides MOS obtained from starch enzymatic hydrolysis we studied the structural complexity of branched malto/isomalto-oligosaccharides (MIMOS) [1]

Results and discussion

Number of potential MIMOS structures for each DP

Each glucose unit has two potential (α -1,4 m or α -1,6 i) linking site. Therefore the number of DP2 isomers is 2. Each of the DP2 isomer has three sites available for branching. For each DP+1 increment the number of will be the product of the DP isomers with the number of DP linking site minus the number of identical obtained structures. With each increment of the degree of polymerization DP(n) the number of potential isomer N of DP(n) increases as follows:

$$N(n) = 2n! + [(n-2)! + 2n-3 \cdot (n-3)!] + [(n-3 + 2n-3 \cdot (n-3)! + [n-4 + 2n-4 \cdot (n-3)!] \dots] \text{ etc}$$

(linear) (1st branch) (2nd branch) (3rd branch) .

The number of isomers grow exponentially with the DP.

Calculation:

The calculated number of potential discrete structure in each DP fraction follows a Catalan [2] binary tree sequence [3].

For increasing DP the number of potential structures of each DP groups is equal to:

$$(2n \text{ choose } n)/(n+1)!/(n!(n+1)!)$$

The number of isomer of DP(n) N is a Catalan number Cn.



$$C_n = \frac{1}{n+1} \binom{2n}{n} = \frac{(2n)!}{(n+1)!n!} \quad \text{for } n \geq 0$$

Eugène-Charles Catalan (1814-1894)

The table provides the calculation of the potential isomers numbers Cn for each oligosaccharidic DP up to Dp 22. The number Cn is the sum of the numbers of isomers for each added branched monomer unit (BMU) for each DP line the DP line (e.g. the number Cn=14 of the DP4 is the sum 1+3+5+5+0 of the BMU line).

Each number in the table is the sum of the line endind over it. (e.g. for DP3/ BMU2 the number 2 is the sum of DP2 line 1+1+0 and for DP10/BMU2 the number 44 is the sum of 1+8+35 of the DP9 line; or the number 440 at the DP 13/BMU3 is the sum 1+12+77+350 of the DP13 line endind over)

It is interesting to note that common syrups displaying DP values (typically up to DP20) could contain more than 6 billions different types of unique oligosaccharidic structures.

Glossary:

Glucose Reducing end

MOS : Malto Oligosaccharides α (1->4)

IMOS : IsoMalto Oligosaccharides α (1->6)

MIMOS : Malto-IsoMalto Oligosaccharides

DP : Degree of Polymerization

BMU : Branched monomeric unit

Ref.:

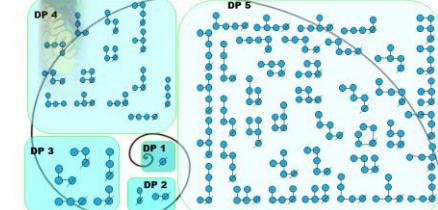
[1] Bliard, C., Martinez, A. (2008). Analyse prédictive des structures potentielles des deadrines MOS et MIMOS. SCF Grand Est Vth meeting of the SCF GE. Vandoeuvre les Nancy, France, 16th of April.

[2] E.C. Catalan, Note sur une équation aux différences finies, J. Math. Pures Appl. 3 (1838) 508-516.

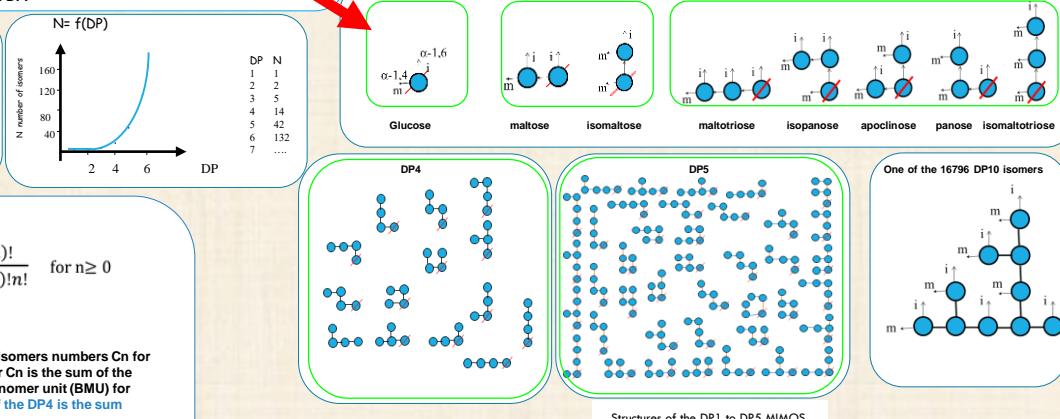
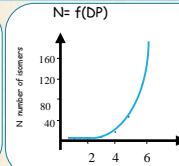
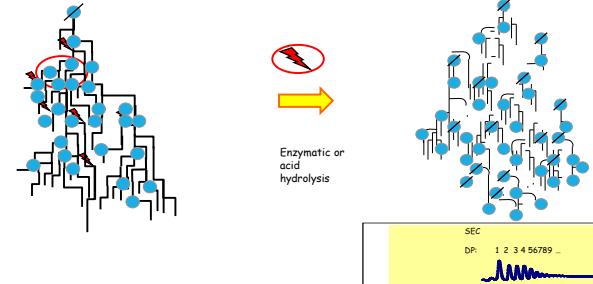
& (b) d'Alvarez, 1839, p.94.

[3] Jean-Christophe Aval, Multivariate Fuss-Catalan numbers, Discrete Mathematics 308 (2008) 4660 - 4669.

Billions of sugars in a spoonful of syrup !



Enzymatic or acid hydrolysis of glucose storage polysaccharide providing syrups of dextrin mixtures



Structures of the DP1 to DP5 MIMOS

DP	Cn	BMU																						C. Bliard 28/03/12												
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22													
1	1	1																																		
2	2	1	1	0																																
3	5	1	2	2	0																															
4	14	1	3	5	5	0																														
5	42	1	4	10	14	14	0																													
6	132	1	6	14	28	42	42	0																												
7	429	1	8	20	48	90	132	132	0																											
8	1430	1	27	75	165	297	426	426	0																											
9	4862	1	50	110	270	577	1001	1430	1430	0																										
10	16796	1	98	244	514	1209	2003	3003	4043	4863	4863	0																								
11	58745	1	10	54	208	637	1638	3640	7077	11934	16796	16796	0																							
12	208012	1	11	61	273	910	2540	6180	1520	2519	41299	58781	58781	0																						
13	742000	1	12	77	350	1260	3808	9996	23762	48465	90440	140232	200812	200812	0																					
14	2674400	1	13	90	440	1730	5529	15504	36740	87210	177595	326874	742900	742900	0																					
15	960485	1	14	108	544	2344	7750	23756	62070	149120	326874	65775	118940	193150	2674400	3724400	0																			
16	3303760	1	15	125	663	2907	8065	33911	95091	245157	572033	122783	241442	434593	702040	908485	908485	0																		
17	1294497	1	16	138	708	3795	14384	48279	14410	38097	961403	2187385	460351	884745	1596798	2662692	35357670	35357670	0																	
18	4773807	1	17	152	950	4655	19012	67298	21109	56027	156275	374940	833070	1779845	3326652	5892949	94387120	129647970	129647970	0																
19	1767263190	1	18	170	1120	5775	24797	9300	30500	90475	249675	621021	1495720	218809	4515730	1248200	2183492	2183492	47763670	47763670	0															
20	6564120420	1	19	188	1309	7084	33785	12370	42570	133205	379879	12001500	564482	1218076	24564720	46393880	11893190	12623440	12623440	1767263190	1767263190	0														
21	24466267020	1	20	208	1518	8602	40480	164450	59300	1924060	572399	1573798	402051	9676800	18381910	46399188	92798370	179909504	305994040	65415240	65415240	1133802610	1133802610	24466267020	24466267020	0										
22	95402563640	1	21	210	1748	10100	50836	215280	807304	273130	845420	241500	64512240	16128060	37962973	149321600	177105360	451574910	654168995	1133802610	1133802610	179909504	179909504	24466267020	24466267020	0										