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

C. Bliard

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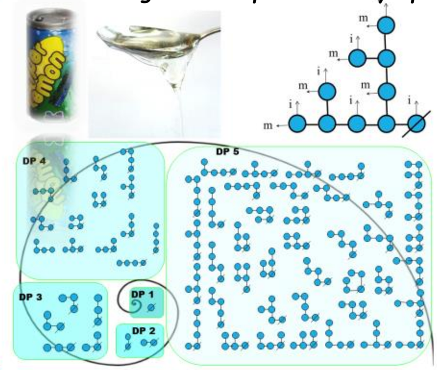
**Abstract** :

Random clivage 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 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).

**Billions of sugars in a spoonful of syrup !**



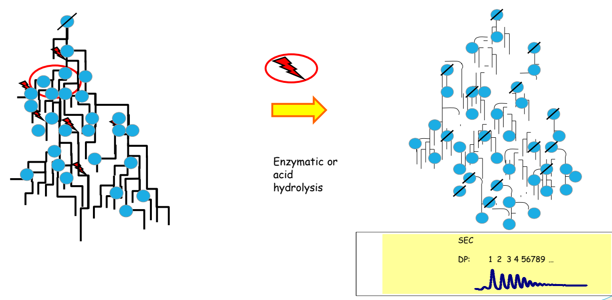

**Introduction:**

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

maltosyl- (m) isomaltosyl- (i) Poly-malto-isomalto saccharide

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]

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




**Results and discussion**

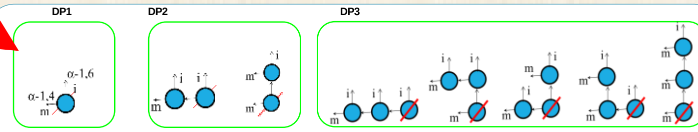
**Number of potential MIMOS structures for each DP**

Each glucose unit has two potential ($\alpha$-1,4 m or $\alpha$–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-1 + [(n-2) + 2n-3 *(n-3)] + [(n-3 + 2n-3 *(n-3)] + [n-4+ 2n-4 (n-3) …] …etc

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

The number of isomers grow exponentially with the DP.




Glucose maltose isomaltose maltotriose isopanose apoclinose panose isomaltotriose

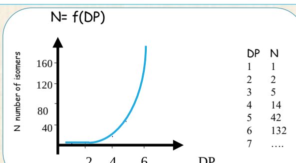
**Calculation**:

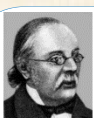
The calculated number of potential discrete structure in each DP fraction follows a Catalan [2] binary tree sequence [3].

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

(2n choose n)/(n+1) = (2n)!/(n!(n+1)!)

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

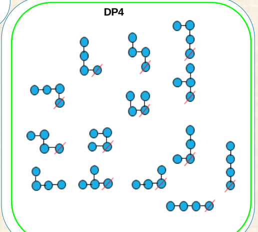


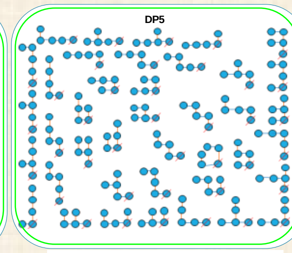
$$C_n = \frac{1}{n+1}\binom{2n}{n} = \frac{(2n)!}{(n+1)!\,n!} \quad \text{for } n \geq 0$$

*Eugène-Charles Catalan (1814-1894)*

**DP4**

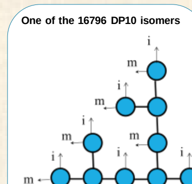


**DP5**



Structures of the DP1 to DP5 MIMOS

**One of the 16796 DP10 isomers**




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 billons different types of unique oligosaccharidic structures.

**Calculation chart of the potential Numbers (Cn) of branched polymers structures for increasing DP as a function of branch Nb (BMU)**

| DP | Cn \ BMU | 0 | 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 | 0 | | | | | | | | | | | | | | | | C. Bliard 28/03/12 | | | | | |
| 2 | 2 | 1 | 1 | 0 | | | | | Each Nb in the table is the sum of the line from \BMU till the number just above | | | | | | | | | | | | | | | |
| 3 | 5 | 1 | 2 | 2 | 0 | | | | | | | | | | | | | | | | | | | |
| 4 | 14 | 1 | 3 | 5 | 5 | 0 | | | The Nb Cn is the sum of the line | | | | | | | | | | | | | | | |
| 5 | 42 | 1 | 4 | 9 | 14 | 14 | 0 | | | | | | | | | | | | | | | | | |
| 6 | 132 | 1 | 5 | 14 | 28 | 42 | 42 | 0 | | | | | | | | | | | | | | | | |
| 7 | 429 | 1 | 6 | 20 | 48 | 90 | 132 | 132 | 0 | | | | | | | | | | | | | | | |
| 8 | 1430 | 1 | 7 | 27 | 75 | 165 | 297 | 429 | 429 | 0 | | | | | | | | | | | | | | |
| 9 | 4862 | 1 | 8 | 35 | 110 | 275 | 572 | 1001 | 1430 | 1430 | 0 | | | | | | | | | | | | | |
| 10 | 16796 | 1 | 9 | 44 | 154 | 429 | 1001 | 2002 | 3432 | 4862 | 4862 | 0 | | | | | | | | | | | | |
| 11 | 58786 | 1 | 10 | 54 | 208 | 637 | 1638 | 3640 | 7072 | 11934 | 16796 | 16796 | 0 | | | | | | | | | | | |
| 12 | 208012 | 1 | 11 | 65 | 273 | 910 | 2548 | 6188 | 13260 | 25194 | 41990 | 58786 | 58786 | 0 | | | | | | | | | | |
| 13 | 742900 | 1 | 12 | 77 | 350 | 1260 | 3808 | 9996 | 23256 | 48450 | 90440 | 149226 | 208012 | 208012 | 0 | | | | | | | | | |
| 14 | 2674440 | 1 | 13 | 90 | 440 | 1700 | 5508 | 15504 | 38760 | 87210 | 177650 | 326876 | 534888 | 742900 | 742900 | 0 | | | | | | | | |
| 15 | 9694845 | 1 | 14 | 104 | 544 | 2244 | 7752 | 23256 | 62016 | 149226 | 326876 | 653752 | 1188640 | 1931540 | 2674440 | 2674440 | 0 | | | | | | | |
| 16 | 35357670 | 1 | 15 | 119 | 663 | 2907 | 10659 | 33915 | 95931 | 245157 | 572033 | 1225785 | 2414425 | 4345965 | 7020405 | 9694845 | 9694845 | 0 | | | | | | |
| 17 | 129644790 | 1 | 16 | 135 | 798 | 3705 | 14364 | 48279 | 144210 | 389367 | 961400 | 2187185 | 4601610 | 8947575 | 15967980 | 25662825 | 35357670 | 35357670 | 0 | | | | | |
| 18 | 477638700 | 1 | 17 | 152 | 950 | 4655 | 19019 | 67298 | 211508 | 600875 | 1562275 | 3749460 | 8351070 | 17298645 | 33266625 | 58929450 | 94287120 | 129644790 | 129644790 | 0 | | | | |
| 19 | 1767263190 | 1 | 18 | 170 | 1120 | 5775 | 24794 | 92092 | 303600 | 904475 | 2466750 | 6216210 | 14567280 | 31865925 | 65132550 | 124062000 | 218349120 | 347993910 | 477638700 | 477638700 | 0 | | | |
| 20 | 6564120420 | 1 | 19 | 189 | 1309 | 7084 | 31878 | 123970 | 427570 | 1332045 | 3798795 | 10015005 | 24582285 | 56448210 | 121580760 | 245642760 | 463991880 | 811985790 | 1289624490 | 1767263190 | 1767263190 | 0 | | |
| 21 | 24466267020 | 1 | 20 | 209 | 1518 | 8602 | 40480 | 164450 | 592020 | 1924065 | 5722860 | 15737865 | 40320150 | 96768360 | 218349120 | 463991880 | 927983760 | 1739969550 | 3029594040 | 4796857230 | 6564120420 | 6564120420 | 0 | |
| 22 | 91482563640 | 1 | 21 | 230 | 1748 | 10350 | 50830 | 215280 | 807300 | 2731365 | 8454225 | 24192090 | 64512240 | 161280600 | 379629720 | 843621600 | 1771605360 | 3511574910 | 6541168950 | 11338026180 | 17902146600 | 24466267020 | 24466267020 | 0 |

**Glossary:**

Glucose Reducing end

MOS : Malto Oligosaccharides $\alpha$ (1->4)

IMOS : IsoMalto Oligosaccharides $\alpha$ (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 dextrines MOS et MIMOS. "SCF Grand Est V" Fifth meeting of the SCF GE. Vandoeuvre les Nancy, France, 15th of April.

[2]E. C. Catalan, Note sur une équation aux différences finies, J. Math. Pures Appl. 3 (1838) 508-516. & (ibid) 4 (1839), 91-94.

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

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