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The example of multiply branched glycans
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In the depth of oligosaccharidic structural complexity
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Abstract:
Random cleavage of branched reserve polysaccharides composed of two different (maltotriose, m) and (isomaltohexose, 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 hybridization 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 DP(2), 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 (maltotetraose) chains branched on each other in a cascade of α-1,6 (isomaltohexose) branches. Chains with molecular sizes of 80 kDa can be synthesized. Enzymatic or acid endo-lisis liberates malto-isomaltodextran (MMOD) of various degrees of polymerization (DP). Unlike oligosaccharides obtained by degrading linear polysaccharides each DP fraction contains a multiplicity of variously branched structures.

Results and discussion:
Number of potential MMOD 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 DP 2 isomer has three sites available for branching. For each DP1 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) = 2^n + 1 + (n+2) - 3*(n-2) + [n*(n+3) - 3*(n+2)] + [n*(n+3) - 2*(n+4) - (n+3)] etc

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

The number of isomers grows exponentially with the DP.

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

For increasing DP the number of potential structures of each DP groups are equal to:
(2n choose n)/(n+1) = (2n)!/(n!(n+1)!) The number of isomers of DP(n) N is a Catalan number Cn.

Glucose storage polysaccharides amylopectin or glycogen are huge polysaccharides composed of α-1,4-linked maltotetraose chains branched on each other in a cascade of α-1,6 isomaltohexose branches. Chains with molecular sizes of 80 kDa can be synthesized. Enzymatic or acid endolysis liberates malto-isomaltodextran (MMOD) of various degrees of polymerization (DP). Unlike oligosaccharides obtained by degrading linear polysaccharides each DP fraction contains a multiplicity of variously branched structures.

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 Dp line ending over it. (e.g. for DP3/ BMU2 the number 2 is the sum of DP line 1+1+0 and for DP10/BMU7 the number 44 is the sum of 1+3+5+0 of the DP3 line, or the number 640 at the DP 13 /BMU3 is the sum 1+12+77+360 of the DP13 line ending over it).

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 : Maltol Oligosaccharidic α (1->4)
IMOS : Isomaltol Oligosaccharidic α (1->6) MIMOS : Malto-Isomalto Oligosaccharidic
DP : Degree of Polymerization
BMU : Branched monomer unit

Ref:

Glossary:
MOS : Maltol Oligosaccharidic α (1->4)
IMOS : Isomaltol Oligosaccharidic α (1->6) MIMOS : Malto-Isomalto Oligosaccharidic

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