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A Mathematical Characterization of Monosaccharides

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Abstract

In this paper, we find a new characterization of monosaccharides by means of mathematical tools. To be more precise, we correspond a barcode to any epimer in each monosaccharide which can carry all its important information. For any natural number α, we define monosaccharides at level α and by a mathematical proof we specify the number of monosaccharides at level α. We also specify which epimers have the same osazone.

1 Introduction

Carbohydrates occur in many living organisms. The sugar and starch in food and the cellulose in wood and paper are nearly pure carbohydrates.

One of the major classes of substances common to living systems are carbohydrate so these compounds as very familiar to us that we call many of them as sugar [1,2]. The task of relating carbohydrate configurations to name requires either a world class memory or an easily recalled mnemonic. The mnemonic device that serves us well was popularized by the

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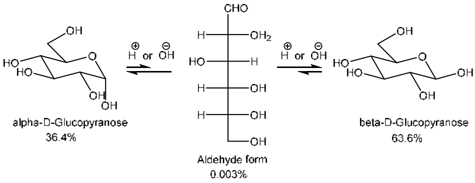
husband-wife Louis Fieser and Mary Fieser at Harvard University in their 1956 textbook [1]. Previously, the list and bibliography of chemical mnemonic devices has been reported [3]. Ciphered formulas in carbohydrate chemistry describe the use of schematic formulas as an aid to rapidly representing configurations for monosaccharides [4]. Understanding the nomenclature and the stereochemical relationships between different monosaccharides can be difficult for students. One of the important topics suggested to be covered in undergraduate education by BIO2010 is carbohydrate chemistry [5]. With the rise of a new era of glycomics, carbohydrates are increasingly being important especially in the pharmaceutical industries [6]. Monosaccharides especially aldohexoses as well as aldopentoses exist as an equilibrium mixture with their cyclic hemiacetal forms in which the later strongly predominate. In fact, representatively, in aldohexose, any of five hydroxy groups could add to the aldehyde carbonyl group (Scheme 1). However, the five and six-membered rings are preferred [7]. Monosaccharide such as glucose, exists primarily as the pyranose form (six-membered ring), instead, fructose forms both fructopyranose (six-membered) and fructofuranose (five-membered ring) equilibrium mixture in solution [7]. If the carbonyl function in aldoses and/or ketoses undergoes reduction reaction furnishes alditol and also condensation reaction with amine, alcohol or thiol and etc., converts to monosaccharide’s linear derivative [8-14]. There are different projections for the structure of the open chain and the cyclic form of β–D–glucose as representative (Fig. 1) [15,16].

One of the major obstacles in teaching carbohydrate chemistry is getting a handle on their name/structure and stereochemical relationships. Hunsen M. [17] reported using a cyclic representation of both D and L monosaccharides, named monosaccharide cycles and a method for determining the stereochemical relationships of all (both D and L) monosaccharides [17]. Arita and Tokimatsu [18] reported the stereo parities of four chiral positions (from C5 to C2) for D-hexose and D-pentose sugars. Based on our new monosaccharides barcoding (Fig. 2) [19], and their applications for discover carbohydrates osazone chart (Fig. 3) [20] and carbohydrates epimeric chart (Fig. 4) including have a centrosymmetric nature in epimeric diagram for carbohydrates (Fig. 5) [21].

In this paper, for any natural number α, we define the monosaccharides at level α. Our definition yields us to get a new characterization of the aldoses and ketoses which can find in nature or we can make them in laboratory. We finally show that for any natural number $\alpha \geq 2$, there exist $2^{\alpha-2}$ sets of aldoses and ketoses which their elements have the same osazone in Fischer projection.

We notice that although our mathematical results show that the monosaccharides can be made at any level, so far only quite limited (having maximum six carbon atoms in their carbon chains) sugar has been obtained in nature and higher carbon monosaccharides in laboratory.



Scheme 1. Representatively, open-chain and pyranose forms of D-glucose (Reproduced with permission from ref. [7]).

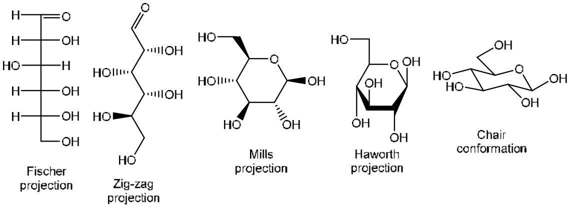


Figure 1. Representatively, different projections for the structure of D-glucose.

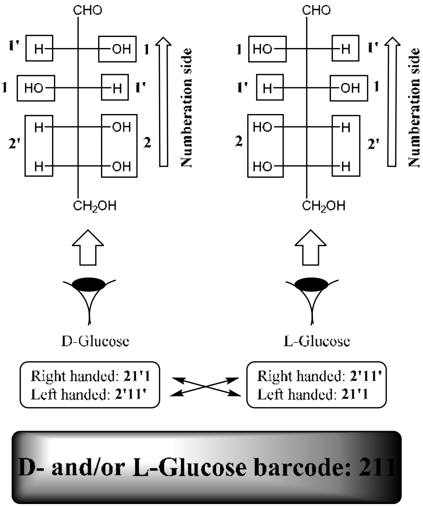


Figure 2. Barcode of D and L-glucose as representative [19].

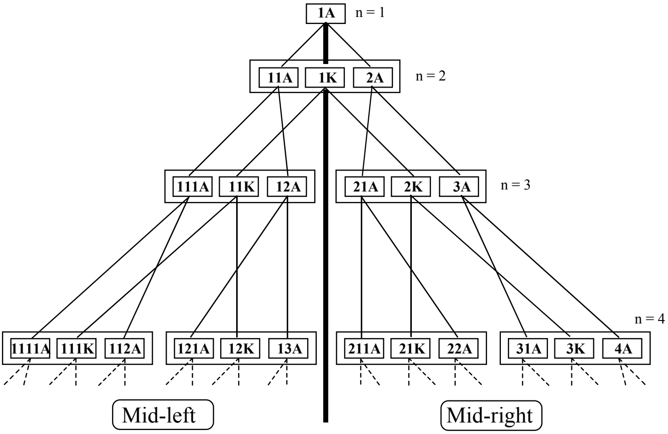


Figure 3. New presented triangular osazone diagram (chart) for carbohydrates for the identification and determination of a pair aldose and a ketose that make the same osazone (A = Aldose (black) and K = Ketose (red)) [20].

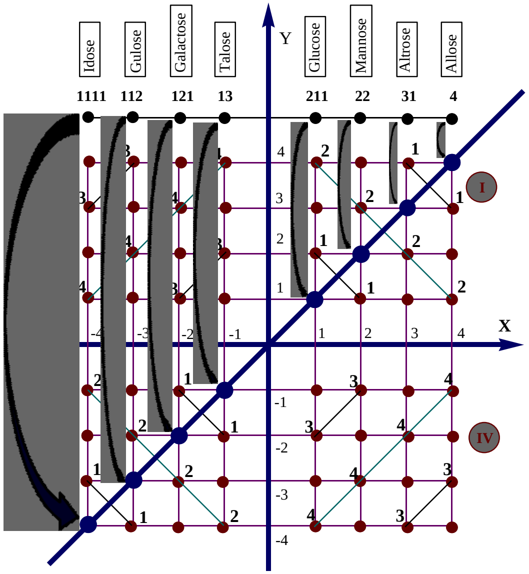


Figure 4. Representatively, an epimeric diagram for aldohexoses [21].

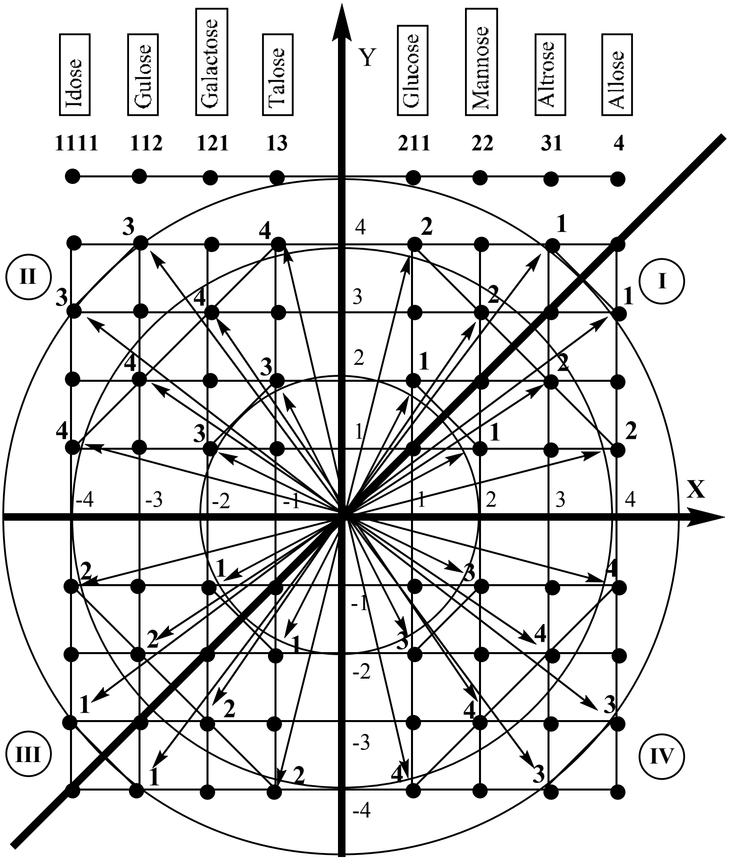


Figure 5. Representatively, a centrosymmetric case in epimeric diagram for aldohexoses [21].

Let α be a natural number. An aldose is *at level* α if in the stereogenic chiral center of its Fischer projection appears α OH groups. An aldose at level α is represented by $(d_1, d_2, \dots, d_n)A$ in which $1 \leq n \leq \alpha$, $d_i \geq 1$ for each $1 \leq i \leq n$ and $\sum_{i=1}^{n} d_i = \alpha$.

In Figure 3, the authors denote any aldose $(d_1, d_2, \dots, d_n)A$ at level α by $d_1d_2 \dots d_nA$, but this barcode is not well-defined if we have an aldose at level α where $\alpha \geq 10$. For example the aldose $12A$ represents simultaneously $(1, 2)A$ at level 3 and $12A$ at level 12.

This is the reason why we use from new barcodes for specifying aldoses. In order to get more understanding of the new barcode, set $\alpha = 2$. Then the aldoses at level 2, by the definition are

$(d_1, d_2)A$ where $d_1 + d_2 = 2$ and d_1A where $d_1 = 2$. In the first case the only possibility is $d_1 = d_2 = 1$; and hence we have two aldoses $(1, 1)A$ and $2A$ as in Figure 3.

Another example, set $\alpha = 3$. Then all aldoses at level 3 are $(d_1, d_2, d_3)A$, $(d_1, d_2)A$, d_3A by the definition. Thus in this case we have four possibilities

(1) $d_1 = d_2 = d_3 = 1$ for the first representation,

(2) $d_1 = 1$, $d_2 = 2$ for the second representation,

(3) $d_1 = 2$, $d_2 = 1$ for the second representation,

(4) $d_1 = 3$ for the third representation.

Therefore we have four aldoses $(1, 1, 1)A$, $(1, 2)A$, $(2, 1)A$ and $3A$. The Fischer projection of an aldose $(d_1, d_2, \dots, d_n)A$ at level α is as follows.

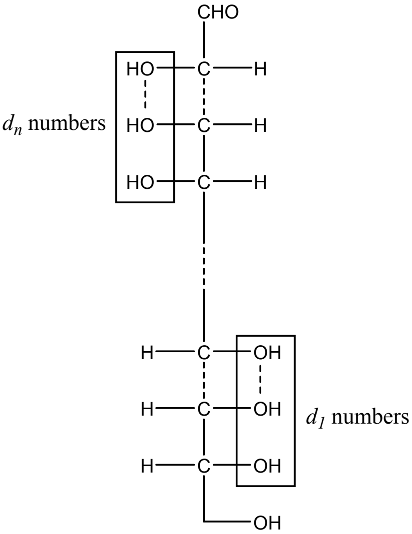


Figure 6. A hypothetical carbohydrate formula of an aldose.

Similarly, a ketose is *at level* α if in the stereogenic chiral center of its Fischer projection appears α -1 OH groups. A ketose at level α is represented by $(d_1, d_2, \dots, d_n)K$ in which $1 \leq n \leq \alpha - 1$, $d_i \geq 1$ for each $1 \leq i \leq n$ and $\sum_{i=1}^{n} d_i = \alpha - 1$.

As we mentioned for aldoses, the barcodes for ketoses based on Figure 3, is not well-defined in general. The authors denote any ketose $(d_1, d_2, \dots, d_n)K$ at level α by $d_1d_2 \dots d_nK$.

For example $11K$ represents simultaneously the aldoses $(1, 1)K$ at level 3 and $11K$ at level 12.

In order to get more understanding of the new barcode, set $n = 2$. Then we have only one aldose at level 2 is $1K$.

Another example, set $\alpha = 3$. Then all ketoses at level 3 are $(d_1, d_2)K$ and d_1K; and hence we have $d_1 = d_2 = 1$ for the first one and $d_1 = 2$ for the second so that we have two aldoses $(1, 1)K$ and $2K$ as in Figure 3.

The Fischer projection of a ketose $(d_1, d_2, \dots, d_n)K$ at level α is as follows.

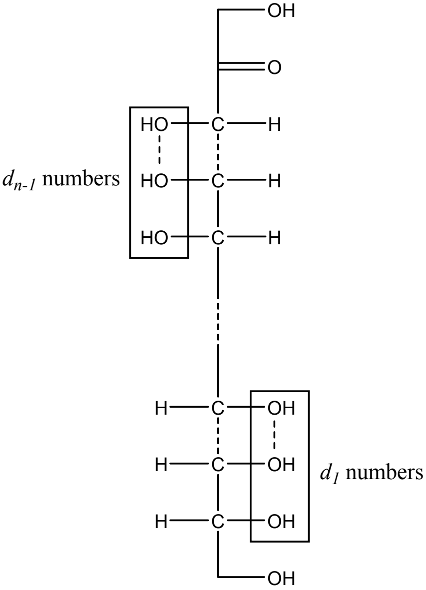


Figure 7. A hypothetical carbohydrate formula of a ketose.

For any natural number $\alpha \geq 2$, the following theorem tells us how many aldoses and ketoses at level α exist.

Theorem 1.1. *For any natural number α, with $\alpha \geq 2$, there exist $2^{\alpha-1}$ aldoses and $2^{\alpha-2}$ ketoses at level α.*

Proof. We proceed by induction on α. The case where $\alpha = 2, 3, 4$ follows by Figure 3. Now, suppose inductively, that $\alpha \geq 5$ and the result has been proved for all values smaller than α. By the induction hypothesis, we have $2^{\alpha-2}$ aldoses and $2^{\alpha-3}$ ketoses at level $\alpha - 1$. We observe that any aldose $(d_1, d_2, \dots, d_n)A$ at level $\alpha - 1$ constructs two aldoses $(d_1, d_2, \dots, d_n + 1)A$ and $(d_1, d_2, \dots, d_n, 1)A$ at level n (see Figure 6). Thus $2 \times 2^{\alpha-2} = 2^{\alpha-1}$ aldoses at level α induce by the aldoses at level $\alpha - 1$. Now, we should show that these are all aldoses at level α. To do this, assume that $(d_1, d_2, \dots, d_n)A$ is an arbitary aldose at level α. Then we have two cases. Case (1): if $d_n = 1$, then $(d_1, d_2, \dots, d_n)$A is obtained by the aldose $(d_1, d_2, \dots, d_{n-1})A$ at level α-1 which we have considered it in the first argument. Case 2: assume that $d_n > 1$. In this case, $(d_1, d_2, \dots, d_n)A$ induces by the aldose $(d_1, d_2, \dots, d_n -1)A$ at level $\alpha - 1$ which we have again considered it in the first argument. In view of Fig. 7, a similar proof applies for the numbers of ketoses at level α.

For any natural number $\alpha \geq 2$, the following theorem tells us how many aldoses and ketoses have the same osazone.

Theorem 1.2. *For any natural number $\alpha \geq 2$, there exist $2^{\alpha-2}$ sets of aldoses and ketoses at level α which their elements make the same osazone.*

Proof. It is clear by the Fischer projection of aldoses and ketoses that the aldoses $(d_1, d_2, \dots, d_{n-1}, 1)A$ and $(d_1, d_2, \dots, d_{n-2}, d_{n-1} +1)A$ and ketose $(d_1, d_2, \dots, d_{n-1})K$ at level α induce the same osazone. Therefore $\boldsymbol{X}(d_1, d_2, \dots, d_{n-1}) = \{(d_1, d_2, \dots, d_{n-1}, 1)A, (d_1, d_2, \dots, d_{n-1} +1)A, (d_1, d_2, \dots, d_{n-1})\mathrm{K}\}$ is one of the desired sets. Now, if we consider K as the set of all ketoses at level n and O as the set of all sets $\boldsymbol{X}(d_1, d_2, \dots, d_{n-1})$ such that $(d_1, d_2, \dots, d_{n-1})K$ is a ketose at level α, then there exists an injective and surjective function $\Phi: K \rightarrow O$ defined as $\Phi((d_1, d_2, \dots, d_{n-1})K) = X(d_1, d_2, \dots, d_{n-1})$.

This implies that $|K|$ and $|O|$, the cardinal numbers of K and O are equal and so it follows from Theorem 1.1 that $|O| = |K| = 2^{\alpha-2}$.

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