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Commentary

A New Facet of Symmetry in Chemistry and Biochemistry

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Abstract

The phenomenon described below concerns molecules having a content of chirality. A new type of symmetry, complementary to the classical symmetry characterized by a mirror plane of symmetry is revealed. As the latter generates an enantiomeric image, the plane of symmetry of this new type of symmetry generates an identical one. The rank of this new plane of symmetry is lower than mirror plane of symmetry. Arguments from chemistry, biology and practical life are brought in support of this new facet of chiral compounds.

Introduction

Detection and measurement of the physical magnitude called optical activity became a current analysis in chemical laboratories in the first quarter of the eighteenth century [1-4]. An exceptional experiment based on measurement of optical activity was made by Pasteur L [5]. He worked on a specimen of tartaric acid devoid of optical activity (racemic or para-tartaric acid) that had been prepared at industrial level by Kestner (1822), an Alsatian manufacturer Kendall J [6], Derewenda ZS [7]. Dextro-tartaric acid had been discovered by Scheele (1770) in the sediment deposited in the vats during the grape juice fermentation [8,9]. Kestner's specimen had the same chemical properties as tartaric acid discovered by Scheele. However, some physical properties (solubility in water, crystalline form, optical activity, etc.) were different [6]. Pasteur prepared the double salt of sodium-ammonium of para-tartaric acid and then crystallized it. He noticed two types of crystals, that were enantiomorphic with one another. Pasteur separated the two types of crystals and found out that their aqueous solutions were dextrorotary and levorotary, respectively. Consequently, the so-called para-tartaric acid was in fact a racemic mixture, (±)-tartaric acid. Another isomer, devoid of optical activity and not cleavable by any chemical or biological method, was discovered also by Pasteur (1853) and called meso-tartaric acid [6].

Van't Hoff JH [10] & LeBel JA [11] signed the birth certificate of stereochemistry by their hypothesis concerning tetrahedral C atom. However, at that time no scientist in the world could rationally associate structural models with the two enantiomers [12]. In fact, the discovery of Pasteur increased the dilemma of representation, i.e., the relationship between a sample of an optically active compound and the unique, characteristic, structural model possibly assigned to it. This dilemma was solved by X-ray diffraction, i. e., zirconium Kα rays, by sodium rubidium tartrate of the dextrorotary species, and the obtained model Figure. 1A-C was assigned to (+)-tartaric acid [13]. By an impressive coincidence, this configuration of (+)-tartaric acid had been hypothetically attributed by Fischer E [14]. Configuration of chiral centers of (–)-tartaric acid (Figure 1D-F) became also known, by the virtue of the law of enantiomorphism. The nomenclature of the two enantiomers became L-(+)-tartaric and D-(–)-tartaric acid, according to the recommendations of Fischer E [15-17], Rosanoff MA [18] & Wohl A, et al. [19]. The isomers of tartaric acid were structurally correlated with the isomers of glyceraldehyde and other monosaccharides as well as with other chiral compounds [19,12,20].

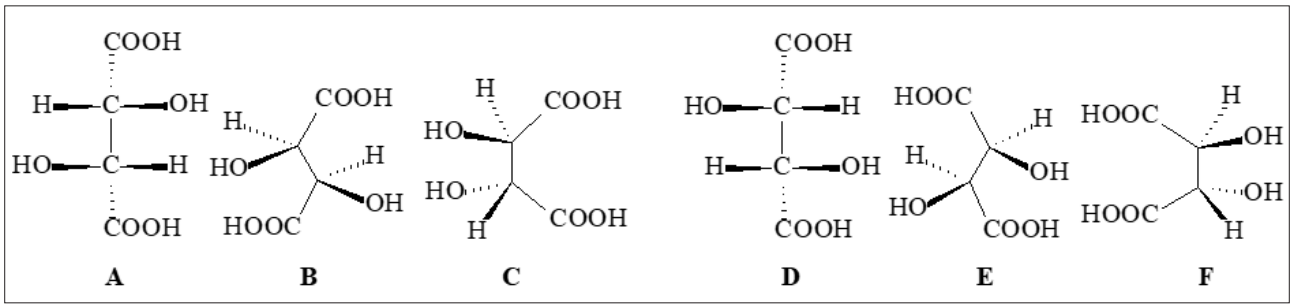

Figure 1: Structural models assigned by Bijvoet JM, et al. [13] to L-(+)-tartaric acid (A, B, C). Configuration of chiral centers of D-(–)-tartaric acid (D, E, F) became known by the virtue of the law of enantiomorphism.

In fact, no other scientist contributed as much as E. Fischer to the transformation of hypothesis of van't Hoff and LeBel in a veritable theory. E. Fischer used a quasi-unique technique, when he elaborated the famous suite of papers concerning the elucidation of monosaccharides structure. His technique consisted in the so-called equalization-deequalization of the two ends of monosaccharides, either by reduction (Na/Hg) to hexitols or by oxidation (nitric acid) to aldaric acids. Then he seemingly returned to the initial compound, also by redox reactions, with the hypothesis in his mind that the two ends have a similar chemical reactivity [21-24].

By this system of reactions, he found out three types of linear aldohexoses:

A. Monosaccharides that reproduced themselves, e.g., D- and L-mannose, D- and L-idose;

B. Monosacharides which besides themselves produced another isomer, e.g., D-glucose produced besides itself a new sugar called L-gulose [25];

C. Monosaccharides that produced a racemic mixture, as if the inner enantiomorphy of their polyol or aldaric acid became externalized in the products, e.g., D-galactose led to D- and L-galactose. Concerning the compounds with identical ends, those produced by (i) and (ii) monosaccharides were optically active, while hexitols and aldaric acids produced by (iii) monosaccharides possessed a mirror plane of symmetry and consequently were optically inactive (meso). All three types of monosaccharides, (i)-(iii), were isomers, and their derivatives with identical ends, hexitols and aldaric acids constituted other two groups of isomers.

Meso compounds (meso-tartaric acid, erythritol, galactitol, allitol, galactaric and allaric acid, etc.) are devoid of optical activity. These compounds possess an even number of atoms in their molecule, they are homodimers. They are characterized by a mirror plane of symmetry drawn between atoms. The tentative of E. Fischer to expand the concept of meso to some heterodimers, e.g., xylitol, ribitol (adonitol), etc., remained a definitive choice in chemical literature. (According to other Fischer's papers concerning chemical synthesis of monosaccharides, as well as to some biosynthesis schemes [26], xylitol and ribitol can be considered as products of reductive dimerization of glycol aldehyde and glyceraldehyde). Fischer found out that both pentitols are devoid of optical activity [27,28], hence they have symmetrical molecules. The mirror plane of symmetry of some heterodimers contains a series of atoms [C-3, H and OH in case of xylitol and ribitol, C-3 and two H in case of 3-deoxyxylitol [29,30] and 3-deoxyribitol [31], etc.]. One can inferr the following rule: all atoms situated within mirror plane of symmetry equally contribute to the chirality of the two halves of the molecule. Hence, we judge heterodimers possessing a mirror plane of symmetry in an idealistic manner: the atoms cut by the mirror plane of symmetry are ignored (or imaginarily eliminated) and what remains is formed of two halves, and involves an even number of C, in fact an even number of atoms. With this amendment, meso compounds can be defined as being formed of two enantiomeric chiral halves. Meso compounds devoid of a mirror plane of symmetry are rigorously formed of an even number of atoms and they are analyzed by Cahn-Ingold-Prelog rules. The result should be an equal number of R and S asymmetric carbons; meso-tartaric acid is (2R,3S or 2S,3R). According to Kelvin and Prelog rules, meso compounds are heterochiral (Kelvin WT [32], Prelog V [33], Cronin J, et al. [34]).

Structural analysis of dextro- and levo-tartaric acid Figure 1 indicates that their molecule is formed of two prochiral identical halves: they are (2R,3R) and (2S,3S), respectively. The same situation is met with D- and L-threitol, D- and L-mannitol, D- and L-iditol, etc. This phenomenon has been disclosed for the first time by Jaeger FM [35] in describing crystals formation by the aggregation of smaller ones (rudimentary or embryonic), to form grown, mature crystals. He used the term twin (or twinning), especially when two such components are united. We have adopted this term and adapted it for chemical and biochemical purposes. We have patterned it as chitwin (chi from chiral plus twin), and we have called the constituents of this group chitwin compounds or chitmers [36-38]. They have been defined as chiral molecules formed of two identical halves. To chitmers possessing an odd number of atoms one applies the same reasoning as for meso ones. Chitmers whose meso isomers are devoid of a mirror plane of symmetry are analyzed by Cahn-Ingold-Prelog rules: the result should be two identical sets of asymmetric carbons.

A chiral molecule can be twinned outwardly, i.e. a simple multiplication, or internally, and in this case a chitwin molecule could be produced. Moreover, in order to describe the symmetry of crystalline systems, Jaeger used the term twinning-plane. This

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reasoning discloses a new type of symmetry at molecular level, and even at macrocosmic one. As mirror plane of symmetry involves two enantiomeric halves, the twinning-plane (we have called it chitwin¬ plane) associates two prochiral identical halves. The chitwin plane has a lower rank than mirror plane of symmetry: L-And D-arabinitol are not chitwin but simply chiral. However 3-keto- and 3-deoxy-arabinitol are chitwin. This concept is supported by many hundreds of natural and artificial compounds, about an order of magnitude bigger than the number of meso compounds. And their multitude is increasing every day. This concept applies especially in chemistry and biology but also in practical life. Many decades after Jaeger's book, they were called C2 symmetrical [39-41]. Chitwin molecules possess a distinctive structure, being formed of two sets of identical chiral carbons and two sets of identical chemical functions. They are internally homochiral and they are C2 symmetrical since they are chitwin. The principle used by E. Fischer to expand the subgroup of homodimeric compounds, also works for chitwin ones although in a more limited manner. In the decades after E. Fischer, chitmers were found among many other families of compounds: amino acids and their derivatives [42,43], carotenoids Iga DP [38], lignans, cyclobutane derivatives, phenolic compounds, alkaloids, terpenoides, lipids, coenzymes based on nucleosides or on cysteine and cysteamine, in oxidized state, homodimeric proteins, palindromes [36,37]. At the same time, chitwin phenomenon has been adopted as a principle of chemical synthesis [44].

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