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On the Impact of Meso compounds and their Isomers: Towards a New Type of Oscillation?

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Abstract *Meso* compounds are of two types: homo- and heterodimers. The quality of *meso* form is apprised either by a mirror plane of symmetry or by application of Cahn-Ingold-Prelog rules, for the molecules devoid of a mirror plane of symmetry (dissymetric). Other elements of symmetry are centre of symmetry and the alternative axis of symmetry. The main subgroup of symmetric compounds is formed of *meso* ones. In this paper we have used arbitrarily *meso* dimers as a reference for comparison with other types of isomers – *C2 symmetrical* (*CTS*), chiral diastereomers (*irrechi*), *constitutional* combinations. However, we possess some arguments for this choice i.e two universal rules concerning *CTS* and *irrechi*. The structure of numerous *meso* heterodimers is presented and the idea is advanced that the atom(s) cut by the mirror plane of symmetry are in fact hidden (masked) by the latter in interaction with polarized light. A question is raised: can the mirror plane of symmetry be saturated (overloaded)? The consequences of a possible affirmative answer to this question are pointed out.

Keywords homodimers, heterodimers, mirror plane of symmetry, meso, C_2 symmetrical combinations, irrechi

Introduction

The knowledge of symmetric compounds, by comparison with assymetric and dissymmetric ones, was dependent of the detection and measurement of optical activity, hence of the discovery and use of polarized light [1,2,3] and the invention of polarimeter [4]. The compound under investigation had to be formed of a unique species of molecules, i.e. to be non-cleavable by chemical or biological methods. Pasteur (1853) discovered the first symmetric compound, that is *meso*-tartaric acid [5,6,7]. Stereochemical theory of tetrahedral and asymmetric (chiral) carbon atom [5,8] led van't Hoff to molecular models based on tetrahedrons which unequivocally represented every chiral carbon atom. (Dots and wedges models of today come from Van't Hoff's models) [9]. Contrary to optically active enantiomers, the dilemma of association van't Hoff's models to Pasteur's sample of optically inactive tartaric acid presented no difficulty, since only one *meso*-tartaric acid is known. The correspondence between the Pasteur's samples of the two enantiomers of tartaric acid and the molecular models suggested by van't Hoff was solved by Fischer [10,11) by pure intuition and experimentally demonstrated by Bijvoet et al., (1951) [12]. Symmetric compounds are dimeric molecules and definition and systematization of these compounds has to take into

consideration some criteria: (i) genesis: they can be formed by a linkage of two chiral (or achiral) combinations or by an indirect (bio)chemical path; (ii) molecular morphology; (iii) chemical composition. These criteria are relative: what really counts is the final result. As molecular morphology the two monomeric units can most often be seen or evidenced in the dimeric state, but this rule has numerous and important exceptions. Chemical composition indicates two types of dimeric compounds: (1) homogenous or even: they contain an even number of every species of component atoms; (2) heterogenous or odd: their molecule is formed of two different sets of atoms and this difference is quantitative or even qualitative [13]. The two sets of chiral carbons in both homogenous and heterogenous dimers can be alternatively fashioned in four different types, corresponding to four types of isomers:

(A) Enantiomeric: they correspond to *meso* compounds. These isomers are considered *meso* by a mirror plane of symmetry, a center of symmetry or an alternative axis of symmetry. Compounds devoid of these elements of symmetry (dissymmetric) are analyzed by Cahn-Ingold-Prelog rules, and the result should be two sets of asymmetric carbons and of chemical functions. (In the latter case one can assert that *meso* molecules are formed of two imaginary identical halves separated by an imaginary mirror plane of symmetry). *Meso* heterodimers are tested exclusively by a mirror plane of symmetry. *Meso* heterodimers discovered/invented by Fischer is a trailblazing achievement illustrated by xylitol [14], ribitol (adonitol) [15], xylaric acid and ribaric acid. Mirror plane of symmetry has to be regarded as an intrinsic property of *meso* compounds. It should be considered both a physical instrument [16] and a natural phenomenon. Mirror plane of symmetry cuts either a bond (bonds) or atoms. Relative to polarized light, mirror plane of symmetry transforms a heterodimer into a homodimer. Two hypotheses might be imagined: (i) it equally distributes the influence of cut atoms between the two enantiomeric chiral halves, or (ii) mirror plane of symmetry simply annihilates the atoms cut by it, or simply masks (hides) them while interacting with polarized light. In either case what remains, as evidenced by polarized light, is an even number of atoms, i.e. a homodimer. According to Kelvin and Prelog theory [17-20] *meso* homodimeric compounds are internally heterochiral, their molecule is formed of two enantiomeric halves. The molecule of all *meso* heterodimers is formed of two enantiomeric halves uniformly linked on an atom or on a polyatomic matrix that can be formed of a carbon linked to two identical (symmetric or enantiomeric) or different (but symmetric) radicals.

(B) Identical: this subgroup refers to C_2 symmetrical (*CTS*) compounds, both to homodimers and heterodimers, and they are all chiral molecules. *CTS* compounds have been defined in relation with an axis and a rotation of 180°. After this maneuver the same atoms should be regained as initially [21,22,23]. *CTS* are the most numerous of these four types of isomers. According to Kelvin and Prelog theory [17-20] *CTS* homodimeric compounds are internally homochiral. Their molecule is formed of two identical halves [23,24]. Of this reason, they could be named also *twin* molecules [25]. The exceptional properties of *twin* (*CTS*) compounds were also noticed by Vickery [26]. Homodimeric *CTS* compounds constitute a chemical duality, the two opposed sides of duality are optical activity, on one hand, and their symmetry. There are two universal rules concerning *CTS* compounds: (i) every *CTS* member, homo- or heterodimer, possesses a real or imaginary *meso* isomer, but the reverse is not necessarily true: some *meso* isomers are devoid of a matching *CTS* representative, at least with the same skeleton; (ii) the molecule of all *CTS* heterodimers is formed of two identical halves uniformly linked on an atom or on a symmetrical polyatomic matrix (formed of a carbon linked to two identical radicals).

(C) The third subgroup is formed of chiral diastereomers which possess a carbon skeleton identical to *meso* and *CTS* i.e. a phenomenon of isoskeletomeric relationship [27]. However, their asymmetric carbons are distributed in an irregular manner in comparison with *meso* or *CTS*. We have preliminarily called them *irrechi* or *irremers* (from *irreg*ular distributed *chi*ral centers). They are much more abundant in natural materials than *meso* isomers. *Meso* isomers are characterized by a 1:1 ratio of numbers of R and S carbons while in *CTS* ones this ratio is n:0, 0:n or 1:1. In *irrechi* combinations the ratio R/S has other values.

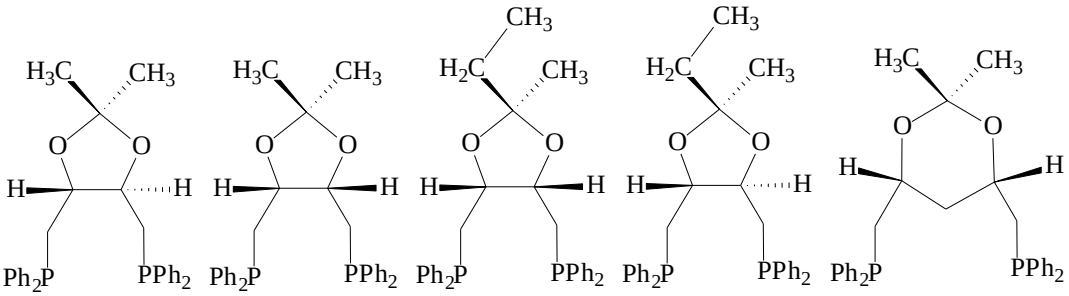
(D) Constitutional (positional) isomers form the fourth subgroup. They are isomer with the preceding ones but their skeleton is different, no structural regularities can be distinguished in their molecules.

We have successfully applied this systematization to the following classes of compounds: (i) carbohydrates; (ii) amino acids, their derivatives and chiral hydroxyacids; (iii) carotenoids (polyprenyl or isoprenoid compounds) and perhydro isoprenoid hydrocarbons; (iv) lignans and neolignans; (v) cyclobutane derivatives; (vi) phenolic compounds; (vii) alkaloids; (viii) terpenoides; (ix) lipids; (x) coenzymes based on nucleosides or on cysteine and cysteamine, in oxidized state; (xi) homodimeric proteins; (xii) palindromes [28-30].

The aim of this paper is to focalize on some *meso* heterodimeric compounds, to indicate the atoms cut by the mirror plane of symmetry and to evaluate the possibility of its overloading (saturation) and the consequences that could arise of this phenomenon.

Natural and Synthetic Meso Compounds

It seemed to us extremely tempting to regard *meso* combinations as a reference for the other three categories, and even possessing the highest rank. Every *CTS* compound is characterized by a real or imaginary *meso* isomer, but the reverse is not necessarily true (Fig. 1). Diphosphine 1 is *CTS*, while diphosphine 2, its isomer, is *meso*. Diphosphine 3 is meso, however diphosphine 4, its isomer with the same skeleton is chiral, non-*CTS*. However, one can construct a *meso* isomer of diphosphine 4, i.e. diphosphine 5, but in the latter case the isokeletometric relationship [27] is walked (Fig. 1). The first *meso* compounds (Fig. 2), both homo- and heterodimers, have been discovered as carbohydrates or their derivatives and no wonder they were used as models and reference for similar compounds of other families [31]. Other symmetrical compounds are also known, however the most numerous are *meso* ones. *Meso* combinations are both natural and synthetic (Figs. 2-4, Table 1) [32]. *Meso* tartaric acid, as well as all *meso* linear polyols and aldaric acids with an even number of carbons are homodimers and their mirror plane of symmetry cuts the bond connecting the two enantiomeric halves. *Meso*-tartaric acid has been found also in spinach leaves and in isolated spinach chloroplasts or as an excreted product [33]. Erythritol occurs in free state in *Protococcus vulgaris* and as an ester with orcellic acid in erythrin [34]. *Meso*-butanediol is produced by fermentation with *Serratia* sp. [35]. Galactitol can be extracted from the yeast *Torula utilis*, grown on wood hydrolysates [36]. Allitol was found in plants of the genus *Itea* [37].



Diphosphine 1 (Diop) (CTS) | **Diphosphine 2 (meso)** | **Diphosphine 3 (meso)** | **Diphosphine 4 (chiral) (non-CTS)** | **Diphosphine 5 (meso)**

Figure 1: Every CTS compound has a real or an imaginary meso isomer but the reverse is not necessarily true

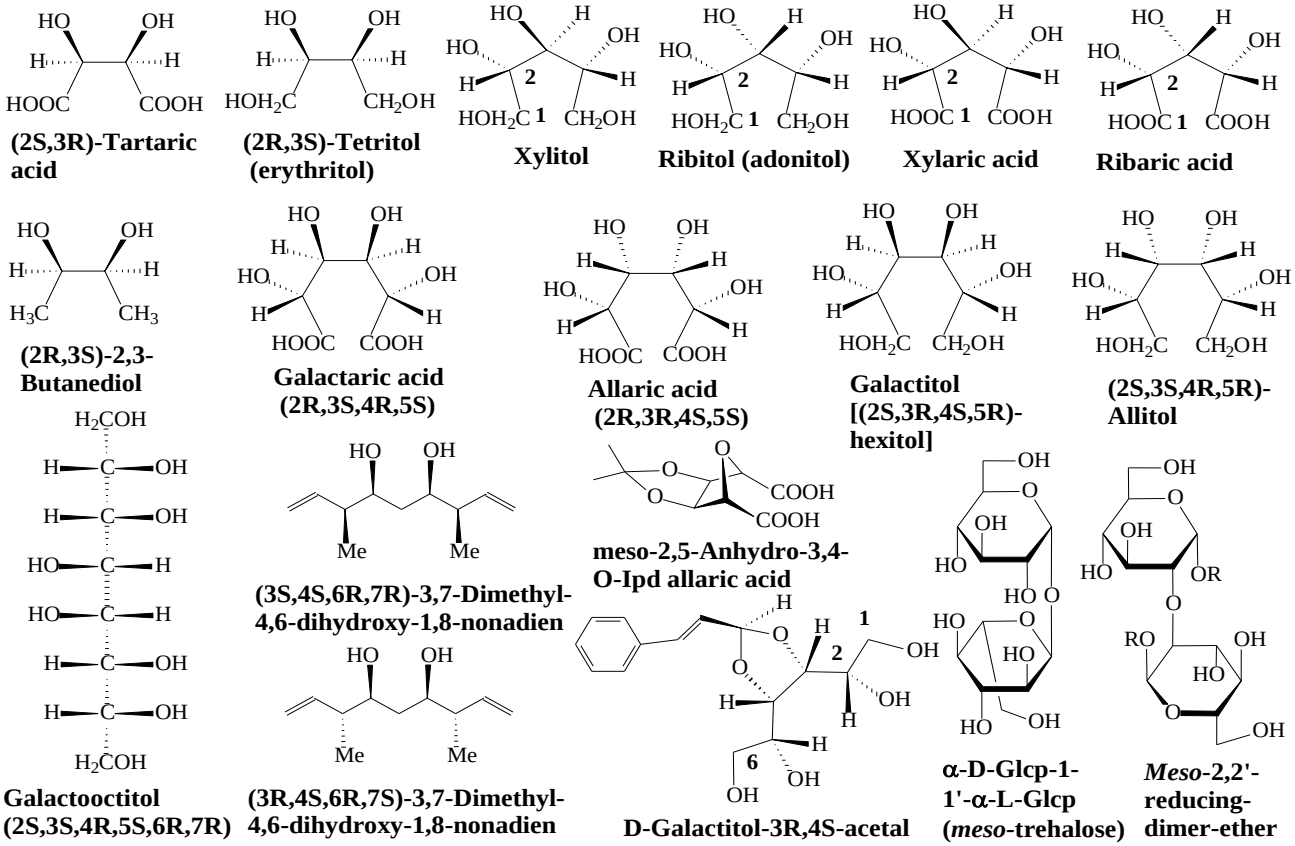


Figure 2: Monosaccharides and their derivatives with meso structure

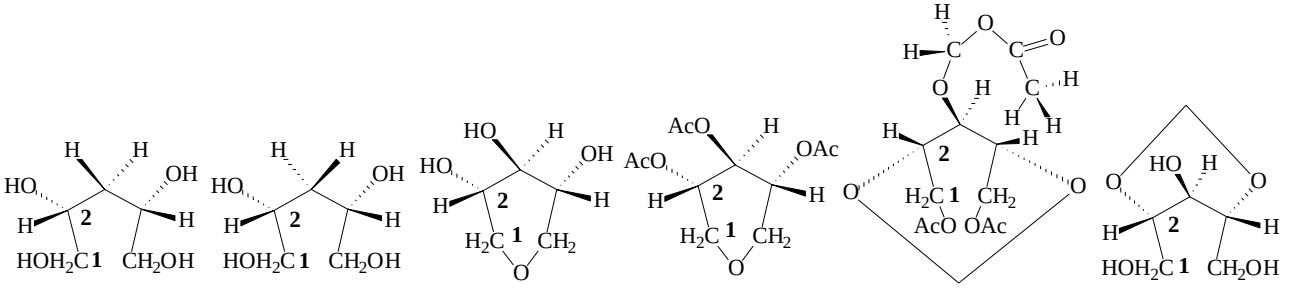


Figure 3: Meso derivatives of xylitol and ribitol

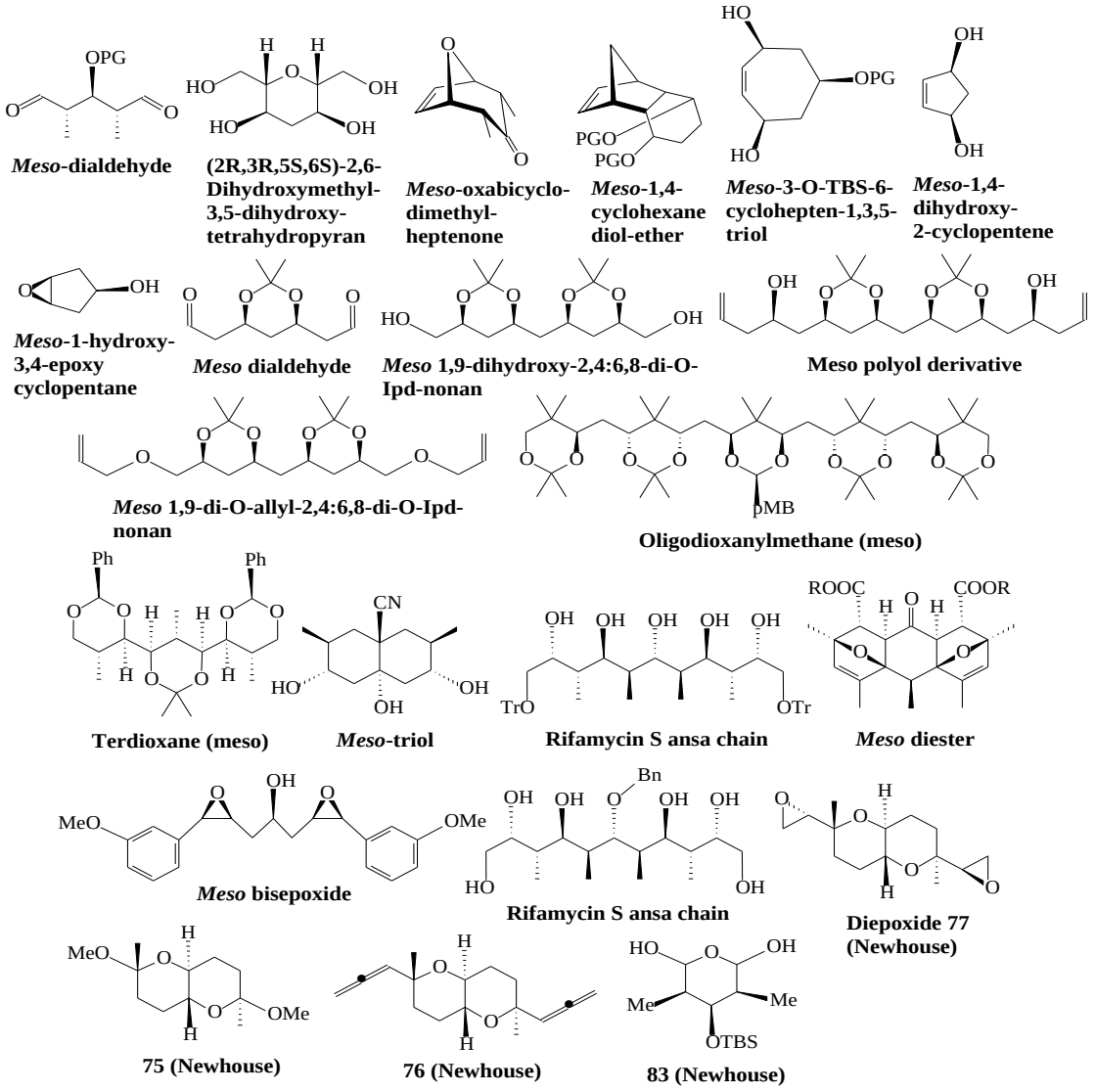


Figure 4: A series of symmetric compounds (compds. 75-77 are centrosymmetric, the others, meso) [32]

Table 1: Atoms cut by the mirror plane of symmetry in heterodimeric *meso* compounds

Compound	Atoms cut by the mirror plane symmetry
Xylitol (or Xylaric acid)	C, H, OH
Ribitol (adonitol) (or Ribaric acid)	C, H, OH
Xylaric acid	C, H, OH
Ribaric acid	C, H, OH
(3S,4S,6R,7R)-3,7-Dimethyl-4,6-dihydroxy-1,8-nonadien	C, H, H
(3R,4S,6R,7S)-3,7-Dimethyl-4,6-dihydroxy-1,8-nonadien	C, H, H
meso-2,5-Anhydro-3,4-O-Ipd allaric acid	O, C, C, H, C, H
D-Galactitol-3R,4S-acetal	CH, CH, CH, C_6H_5
3-Deoxy-xylitol	C, H, H
3-Deoxy-ribitol	C, H, H
1,5-Anhydro-xylitol	O, CH, OH
1,5-Anhydro-xylitol 2,3,4-Tri-O-Ac-1,5-anhydro-xylitol	O, CH, O, C=O, CH

1,5-Di-O-Ac-3-acetoxy-methyl-2,4-methylene-xylitol	CH, H, CH, O, C, O, C=O, CH
2,4-Methylene-xylitol	CH, OH, C, H, H
Meso-dialdehyde	CH, O, PG*
(2R,3R,5S,6S)-2,6-Dihydroxymethyl-3,5-dihydroxy-tetrahydropyran	O, C, H, H
Meso-oxabicyclo-dimethyl-heptenone	O, C, O
Meso-1,4-cyclohexane diol-ether	H, H, C, H, H, C
Meso-3-O-TBS-6-cyclohepten-1,3,5-triol	C, H, O, Si, C, CH
Meso-1,4-dihydroxy-2-cyclopentene	H, H, C
Meso-1-hydroxy-3,4-epoxy cyclopentane	HO, CH, O
Meso dialdehyde	H, H, C, C, CH, CH
Meso 1,9-dihydroxy-2,4:6,8-di-O-Ipd-nonan	H, H, C
Meso polyol derivative	H, H, C
Meso 1,9-di-O-allyl-2,4:6,8-di-O-Ipd-nonan	H, H, C
Oligodioxanylmethane (meso)	CH, CH, C, CH, C, C_6H_4, CH
Terdioxane (meso)	CH, CH, C, CH, CH
Meso-triol	N, C, C, C, OH
Rifamycin S ansa chain	CH, OH
Meso diester	CH, CH, C=O
Meso bisepoxide	CH, OH
Rifamycin S ansa chain	CH, O, C, C_6H_5
83 (Newhouse)	O, CH, O, Si, C, CH

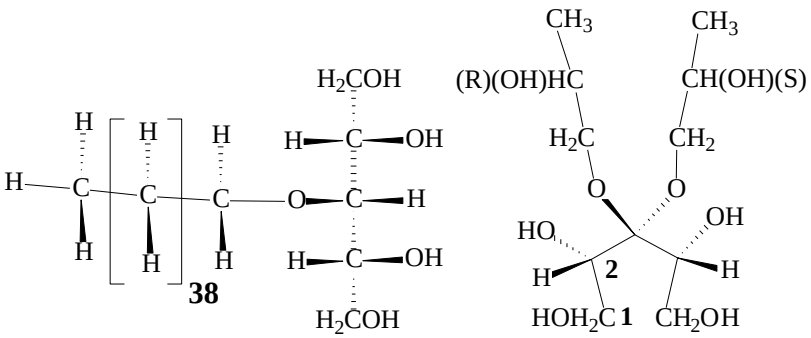
* PG, protecting group; it should be a symmetric group [32].

Xylitol was found in fungi [38] and ribitol in *Adonis vernalis* (15,39). Aldaric acids were obtained by synthesis: allaric acid [40], xylaric and ribaric acid [41,42], galactaric acid [43]. Galaoctitol is also a synthetic product [44-46]. D-galactitol-3R,4S-acetal was found in tender stems of *Cinnamomum cassia* [47]. *Meso* isomers, (3S,4S,6R,7R)-3,7-dimethyl-4,6-dihydroxy-1,8-nonadien and (3R,4S,6R,7S)-3,7-Dimethyl-4,6-dihydroxy-1,8-nonadien, have been synthetized by reaction of 1,3-propanediol and allyl acetate at both ends (double crotylation), in the presence of a complex catalyst based on iridium [48].

Meso derivatives of xylitol and ribitol have been synthesized by chemists specialized in carbohydrate chemistry: 3-deoxyxylitol [49,50] and 3-deoxyribitol [51]; 1,5-anhydro-xylitol, 2,3,4-tri-O-acetyl-1,5-anhydroxylitol [52], 1,5-diacetyl-3-acetoxymethyl-2,4-methylene-xylitol, 2,4-methylene-xylitol [53] etc. *Ent* compounds are usually synthetic products which are enantiomers of natural ones. L-Glucose (*ent*-glucose) was synthesized in order to be included in a new cerebroside, 1-O-β-L-glucopyranosyl-N-palmitoyl-DL-sphingosine [54]. In spite of the fact that both isomers D- and L-glucose (*ent*-glucose) [54] are known, neither *meso*-trehalose (α-D-glucopyranosyl-α-L-glucopyranose) nor their isomeric reducing dimer ether (Fig. 2) have been synthesized.

Towards a new type of oscillations?

Some *meso* derivatives (Fig. 4) were prepared as heterodimeric synthetic chemical precursors [32]. These *meso* chemical precursors are relatively small molecules containing 2-10 asymmetric carbons. At least for some of them a diversity of *CTS*, *irrechi* and even other *meso* isomers can be imagined. The mirror plane of symmetry of *meso* heterodimeric compounds cuts a series of atoms (Table 1) and what remains is a homodimeric entity. Let's suppose that we introduce a pinion fragment alternatively affecting the two halves, due to a kind of saturation of mirror plane of symmetry. One might suppose that in this case optical rotation would oscillate between dextro- and levorotary, and a new type of oscillation would be disclosed. We suggest two alternatives for this effect (Fig. 5): either a voluminous radical or two enantiomeric chiral residues.



3-O-Tetraconta-xylitol **Xylitol derivative**

Figure 5: Possible alternatives to overload the mirror plane of symmetry

Quantum interference has been used to distinguish between constitutional isomers [55]. However, this technique has not been used to other types of isomers, according to our knowledge. Molecular diversity of substituted cycloalkanes presented as constitutional and steric isomers was evaluated by Pólya's theory [56,57]. At least for cyclopropanes and cyclobutanes, three types can be distinguished, apart from constitutional: *meso*, *CTS* and *irrechi* [58]. The four tetramethylcyclobutane isomers presented were the following: two *meso*, one *centrosymmetric* and one *irrechi* [59]. Anticonvulsant isomers of valproic acid [VPA; 2(propyl)pentanoic acid, *meso*] were exclusively constitutional: [VCA, valnoctic acid; 2-ethyl-3-methyl pentanoic acid (*constitutional*)], [DIA, 2-isopropyl-3-methyl butyric acid (*meso* but *constitutional*)], [(R)-PIA, (S)-PIA, 2-isopropyl pentanoic acid (both *constitutional*)], octanoic acid (*constitutional*) [60]. Hence if we take VCA (*meso*) as a reference, its isomer DIA (also *meso*) is in fact *constitutional*. And viceversa, if we take DIA (*meso*) as a reference, its isomer VCA (also *meso*) is *constitutional*. There is no contradiction here but a sheer sample of dialectics.

Conclusions

1. Symmetric dimeric compounds are of two types: homodimeric and heterodimeric. Their type is decided by their chemical composition.
2. Symmetric dimers are of four types: *meso*, C_2 *symmetrical* (*CTS*), chiral distereomeric (*irrechi*) and *constitutional*.
3. A universal rule concerning *CTS* and *irrechi* has been found: every member of this subgroup possesses a real or a possible *meso* isomer, but the reverse is not necessarily true.
4. The following question has been raised with all its consequences: has the mirror plane of symmetry of *meso* heterodimer compounds a finite or an infinite potential.

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