Bermuda Triangle in Chemistry

Dumitru Petru I. Iga\textsuperscript{a,b*}, D. Popescu\textsuperscript{c} and V. I. R. Niculescu\textsuperscript{d}

\textsuperscript{a} University of Bucharest, Former C. I. Parhon, Bulevardul Regina Elisabeta Nr. 4-12, București-030018, Romania.
\textsuperscript{b} University of Oradea, Strada Universității Nr. 1, Oradea-410087, Romania.
\textsuperscript{c} Gh Mihoc-Caius Iacob Institute of Mathematical Statistics and Applied Mathematics of Romania, Academy, Romania.
\textsuperscript{d} Institut de Recherche et Development pour les Lasers, Plasma et Physique de la Radiation, Romania.

Authors’ contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

It is believed that the place called Bermuda triangle is able to hide of human seeing objects entered its area. A Bermuda triangle in chemistry is able to hide (mask) atoms or planar molecular fragments cut by their mirror plane of symmetry, not of human eyes but, of polarized light. A triangular skeleton (frame) has been imagined, possessing the ability to cover many hundreds of molecular formulae, providing the latter refer to aliphatic, or partially aliphatic, compounds, and with a low degree of oxidation. This skeleton (frame) is based on a very general and strong principle, valid in \textit{meso} entities. The idea is advanced that isomers coming up from a molecular formula could be of four types (groups): \textit{meso}, \textit{C}_2 symmetrical (\textit{CTS}), \textit{irrechi} (from \textit{irregular chiral}) and \textit{constitutional} (\textit{constit.}). The following universal rule is revealed: all \textit{CTS} and \textit{irrechi} can be converted to \textit{meso} ones, but the reverse is not true, at least for the same skeleton. At the same time, an impressive number of constitutional natural or synthetic combinations are characterized by at least one real or envisaged \textit{meso} isomer. Thus, from a structural point of view, \textit{meso} isomers are justified as reference compounds. The above mentioned principles have been applied to numerous natural compounds: amino acids, lipids, carbohydrates, nucleosides, vitamins, steroids, alkaloids, hydrocarbons. A mathematical equation sustaining the triangular representation has been proposed. One raises the question which of the four types is the upper. A tentative answer is given to this question.

\*Corresponding author: E-mail: pdiga49@yahoo.com;
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1. INTRODUCTION

The analysis of isomerism phenomena as well as of numerous natural and synthetic compounds disclosed at most four types of isomers: (A) meso, (B) C2 symmetrical (CTS), (C) irregular chiral (irrechi) and (d) constitutional (constit.). We have tried to check an old idea [1,2], concerning the ubiquitous existence of symmetry in nature, especially in physical-chemical and biological systems. We have undertaken an integrative approach based on molecular formula, and an exercise of comparative chemistry, by using meso compounds as structural references. Every molecular formula concerning natural or synthetic compounds, with a significant moiety of an alkane skeleton, and a given level of complexity, might produce the afore mentioned four types (groups) of isomers. In fact, the significance given by us to the four types will become quite obvious from their use and application.

(A) Meso isomers: There are three types of meso compounds [3]; (A1) characterized by a mirror plane of symmetry; at their turn, (A1) are of two types: (A11) the molecule of the first type is formed of two enantiomeric chiral halves uniformly linked with each other [4-6]; (A12) the two enantiomeric chiral halves of the second type are uniformly linked on an atom or on a matrix devoid of handedness, or a matrix characterized by a mirror plane of symmetry [7]; (A2) The second type of meso compounds is devoid of elements of symmetry (dissymmetric compounds) and they have to be analyzed by Cahn-Ingold-Prelog rules [8,9]. Their molecule contains two sets of asymmetric carbons with opposed handedness. (In the latter case one can assert that molecules are formed of two imaginary enantiomeric halves separated by an imaginary mirror plane of symmetry).

Meso isomers are optically inactive (optinactive) due to an internal compensation. The existence of two enantiomeric sides in meso compounds was proved by Fischer and Hertz [10] in an elegant experiment on galactaric acid. They kinetically reduced this acid and the product was a racemic mixture of galacturonic acids. The two enantiomeric acids were separated as strychnine salts and characterized. In this way the internal enantomorphism of meso derivative become externalized. Subsequently, chemists would try to overturn this feature of meso compounds and to predominantly, if not exclusively, prepare one product only [11-14]. Meso heterodimers polyols discovered (or invented) by Fischer – xylitol [15], ribitol (adonitol) [16], xylaric (trihydroxiglutaric) acid, ribaric acid [17] – have been a trailblazing achievement and they turned out to be models for other combinations of the same category. Mirror plane of symmetry has to be regarded as an intrinsic property of meso compounds. It should be considered both a physical instrument and a natural phenomenon. Mirror plane of symmetry hides or exposes or hides or exposes either a bond (bonds) or atoms. Relative to polarized light, mirror plane of symmetry transforms a heterodimer into a homodimer. Mirror plane of symmetry hides (masks) the atoms cut by it from polarized light, and what remains, as evidenced by this physical instrument, is an entity containing an even number of atoms, i.e. a homodimer. Meso heterodimers constitute a chemical duality, the two opposed sides of duality are their heteromeric character, on one hand, and their expression as homodimers, on the other hand. According to Kelvin and Prelog theory [18-20] meso compounds are internally heterochiral. There is a fundamental difference between the mirror plane of symmetry in macrocosmos and at physical-chemical level in microcosmos. In the first case, the mirror plane of symmetry just indicates the limit of the two enantiomeric halves. At physical-chemical level, it can cut atoms and hide them of polarized light. As will be evident of this paper, this spectacular property of mirror plane of symmetry plays an extremely important role in systematization of isomers emerging of the same molecular formula.

(B) C2 symmetrical (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 [21-23], and all CTS compounds are chiral and optically active (optactive). Their molecule is either formed of two identical chiral halves uniformly linked with each other [24,25] or of two identical chiral halves uniformly linked on an atom [25] or on an achiral [25] or CTS matrix [26]. According to Kelvin and Prelog theory [18-20], CTS formed exclusively of two identical chiral halves are homochiral with each other and internally homochiral [23,27]. Of this reason, they could be named also twin molecules [1]. The exceptional
properties of twin (CTS) compounds were also noticed by Vickery [28]. Homodimeric CTS compounds constitute a chemical duality, the two opposed sides of duality are optical activity, on one hand, and their symmetry, on the other hand. There is one universal rule concerning CTS compounds: every member of this group possesses a real or imaginary meso isomer. Two cases should be mentioned. Compounds based on 1,2-diamino-cyclohexane [13,22,29,30] are CTS as long as they are trans. Their cis isomer should be meso only by adopting a planar cycle, as for allo-inositol. Of the six meso isomers of inositol [31,32], five are characterized by 1,4 mirror plane of symmetry, while allo-inositol is devoid of such a plane. Its meso nature can be explained only by a planar structure, hence the mirror plane of symmetry cuts two opposed bonds. (One can write a meso isomer of 1,2-diamino cyclohexane as 1,2-cyclobutane derivative).

The first CTS combinations, the two enantiomers of tartaric acid, have been separated by Pasteur (1848) by crystalization from a racemic mixture that had been prepared by Kestner (1822) [33-35]. Pasteur noticed two types of crystals, that were enantiomorphic with one another. He separated the two types of crystals and found out that their aqueous solutions were dextrorotary and levorotary, respectively. Dextro-tartaric acid had been discovered by Scheele (1770) in the sediment deposited in the vats during the grape juice fermentation [36,37]. 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 [33,34]. Stereochmical theory of tetrahedral and asymmetric (chiral) carbon atom [38,39] led van't Hoff to molecular models based on tetrahedrons which unequivocally represented every chiral carbon atom. By constructing and using these models, van't Hoff expanded the idea of enantiomorphism from crystals to molecules. (Dots and wedges representations of today come from van't Hoff’s models). However, at that time no scientist could rationally associate structural models with the two enantiomers [40]. 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., of zirconium Kα rays, by sodium rubidium tartrate of the dextrorotary species, and the obtained model was assigned to (+)-tartaric acid [41]. By an impressive coincidence, this configuration of (+)-tartaric acid had been hypothetically attributed by E. Fischer (1896) [42]. Configuration of chiral centers of (−)-tartaric acid became also known, by the virtue of the law of enantiomorphism. Configuration of the two enantiomers has been connected with other chiral compounds, beginning with (−) and (+)-glyceraldehyde [43]. A chemical relationship has been found between E. Fischer and his son, H. O. L. Fischer [44,45], due to a derivative of D and L-mannitol prepared by the latter, i.e. 1,2-5,6-di-O-isopropyldene mannitol (CTS). By integration of finding of H. O. L. Fischer in the strategy of E. Fischer, structure elucidation of linear aldohexoses becomes more direct [46].

(C) *Irrechi*: The third subgroup of isomers of meso compounds are also chiral and they are characterized by a molecular skeleton identical to meso and CTS, i.e. a phenomenon of isoskeletomeric relationship [47]. Still, chiral carbons are irregularly distributed in their molecule [48]. E. g. glucitol [17], bicubebin [49], bismurrangain [50], hyboacarpone [26], asarolignans [51], larreacin [52], numerous carotenoids [53,54]. *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) (constit.) isomers form the fourth group. They are isomer with the preceding ones but their skeleton is different. They are either optactive or optinactive. With relatively few exceptions, compounds currently met in living things are constitutional isomers. They are probably the most abundant in natural materials.

An interesting group of constit isomers is formed by a non-uniform linkage of monomers: quadrigemine C [55], aspergilazine A [56], penicillixanthone A, phomoxanthone B, dideacetylphomoxanthone B, ruguloterosin B [57], quadrigemine B [55], taondiol dimer [58,59], numerous carotenoids [53,54].

The application of our systematization to monosaccharides, discovered/invented by Fischer and others, produces the following results. (A) *meso* monosaccharides: galactitol [(2S,3R,4S,5R)-hexitol] [15,60], allitol [(2S,3S,4R,5R)-hexitol] [61-64], galactooctitol [(2S,3S,4R,5S,6R,7R) octitol] [65-67], galactaric acid (2R,3S,4R,5S) [10], allaric acid (2R,3R,4S,5S) [68]. (B) *CTS* monosaccharides:
D-mannitol [(2R,3R,4R,5R)-hexitol], L-mannitol [(2S,3S,4S,5S)-hexitol] D-mannaric acid [(2R,3S,4S,5R)], L-mannaric acid [(2S,3R,4S,5R)] [69], D-iditol [(2R,3S,4S,5R)-hexitol], L-iditol [(2S,3R,4S,5R)-hexitol], D-idaric acid [(2R,3S,4S,5R)], L-idaric acid [(2S,3R,4S,5R)] [70-72]. (C) irrech! monosaccharides: D-glucitol [L-gulitol (2S,3R,4R,5R)-hexitol] [73], L-glucitol [D-gulitol (2R,3S,4S,5R)-hexitol], D-glucaric acid [L-guluronic (2R,3S,4S,5R)], D-glucuronic acid [D-guluronic (2S,3R,4R,5R)], D-altitol [D-talitol (2R,3S,4R,5R)-hexitol], L-altitol [L-talitol (2S,3R,4S,5S)-hexitol], D-altraric acid [D-talaric (2R,3S,4S,5S)], L-altraric acid [L-talaric (2R,3S,4R,5R)] [15,17,70,71,74] and 1,1,1,2,2,3-hexanexehol [75]. (D) constiti: D-hamamelitol [76-78]. Concerning limits and possibilities of reciprocal changing of types mentioned above, both CTS and irrech! can be transformed into meso. Some interesting facts should be mentioned: the molecule of iditols and idaric acids possesses an equal number of R and S carbons, similarly with galactitol, allitol, galactaric and allaric acids. However they are not meso but optactive [31]. The difference can be explained probably by the fact that the molecule of the former is formed of two identical chiral halves and the latter of two chiral enantiomeric halves. The two hydrogen atoms of central methylene of a meso derivative, i.e. 3-deoxyxylitol, 3-deoxyribitol, meso-diaminopimelic acid, etc., are not equivalent. If they are alternatively replaced by a hydroxy function, the products are different. The two central hydrogen atoms of CTS compounds, i.e. 3-deoxyarabinitol, 3-deoxylxylitol, L-L- and D,D-diaminopimelic acid, etc., are equivalent; if they are alternatively replaced by a hydroxy function, exclusively one product is obtained.

The molecular diversity is connected with the following factors: (i) Structures as diamond [79], graphite and fullerenes [80,81] illustrate the best the ability of C atoms to bind with each other. However, all these forms present a very limited structural variety. (ii) What really confer molecular diversity to C combinations is the association of this element with hydrogen and this is evidenced by the remarkable molecular variety of aliphatic hydrocarbons [32,82,83]. Molecular diversity is a physical-chemical magnitude concerning the ability of a compound to present a large number of isomers. (iii) Chemical functional groups, in relative low proportion, also favor molecular diversity. (iv) Aromatic hydrocarbons present the lowest molecular diversity of all organic combinations.

They contain an exceeding number of chemical functions, and they are in a state of advanced oxidation. In fact, they fill an intermediate place between elementary carbon and aliphatic hydrocarbons. Another remarkable feature of aromatic hydrocarbons is the fact that they do not present meso isomers. (v) Molecular diversity increases exponentially with molecular weight [27,83,84]. (vi) Carbon dioxide is a terminal facet of metabolism and combustion of organic compounds. It is characterized by a high chemical inertia. Carbon dioxide has to be attached to a preexisting structure, as a piece of metal in a lathe, and stepwise reduced, the energy of sun playing an essential role in this process called photosynthesis [85].

Our aim have been especially monomeric units [85], but we prove that compounds called by Metzler in this way can also have meso isomers, hence an authentic dimeric character.

2. THE MAJOR METABOLITES CONTAINING A SIGNIFICANT ALKANE MOIETY POSSES AT LEAST ONE REAL OR ENVISAGED MESO ISOMER

A guiding line of this paper is to find out at least one meso isomer for every molecular formula. A serious obstructor to this is an advanced degree of unsaturation. E.g. is impossible to find out a meso isomer for C,H,O (fumaric/maleic acids). However, C,H,O (2,3-dimethyl derivative, etc) has a meso form [48,54] (Fig. 1). Similarly, every tentative to construct a meso isomer of benzene, fails.

However, the thing is possible for xylenes, ethylbenzene, propylbenzene, etc. Also, reduction product of benzene, cyclohexane, presents meso isomers. Naphthalene, similarly to benzene, fails to give meso isomers, decalines instead presents such isomers (Fig. 1).

At least two dozens of isomers with molecular formula C,H,O can be written, just by utilising the consecrated valence of every component element. However, of the envisaged isomers only some present elements of symmetry: two are meso (cis-1,2-dihydroxy-3-amino cyclopropane and cis-2,4-dihydroxy-azetidine), and two are CTS (trans-2,4-dihydroxy-azetidine, two enantiomers), and all the others, including (R)- and (S)-alanine, are constiti.

In the following (Figs. 2-11), the envisaged isomers are presented for a large variety of natural and synthetic compounds.
Fig. 1. Meso isomers of unsaturated (fumaric/maleic acid), aromatic, and the latter’s saturated compounds

2.1 Compounds with Serial Structure

Compounds with serial structure present a large variety of molecular formulas (Figs. 2-4), in agreement with their molecular weight.

2.1.1. Aliphatic hydrocarbons: alkanes, alkenes (cycloalkanes), alkynes (alkadienes)

Of aliphatic hydrocarbons, only alkanes fail to present a triangular meso isomer (Fig. 2). A tentative to evaluate molecular diversity of C₈H₁₈ indicated 18 [84] or 19 (83) isomers. If one take into account optical activity [86], the total number of isomers is 24 and 55, respectively. Of these, one is meso, two are CTS [87] (Fig. 2) and the others are constit. An unequivocal conclusion can be drawn: all alkanes beginning with C₈H₁₈ present at least one meso isomer.

As a representative of C₁₀H₂₀, eicosene can be seen (Fig. 2). The first term according to our reasoning is the meso isomer, cis-1,2-dimethyl cyclopropane [88].

Fig. 2. Meso isomers of saturated and unsaturated hydrocarbons
For C\textsubscript{3}H\textsubscript{7} (alkynes and alkenes) meso isomer of heneicosyne (as cis-1,2-dihexyl-3-hexenyl-cyclopropane) is indicated, the first term being C\textsubscript{3}, cis-1,2-dimethyl-3-vinyl cyclopropane or cis-3,5-dimethyl-1-cyclooctene.

### 2.1.2 Serial compounds with functional groups

For monohydroxylic alcohols there is a meso isomer of eicosanol (9-hydroxymethyl-8,10-dimethyl heptadecane), the first term is C\textsubscript{3}\textsubscript{0} (3,5-dimethyl-4-hydroxy heptane) (Fig. 3). For aldehydes and ketones we introduce meso isomer of heneicosanoid (cis-1,2-dihexyl-3-hydroxy-3-butyln), the first term is C\textsubscript{3}\textsubscript{1} (cis-1,2-dimethyl-3-hydroxy-cyclopropane).

Meso isomer of eicosanoic acid [cis-1,2-bis(hexanol)-3-methyl-cyclopropane] represents organic acids, and the first term is C\textsubscript{3}\textsubscript{2} (cis-1,2-di-hydroxy-cyclopropane). C\textsubscript{3}\textsubscript{2} still, as well as C\textsubscript{4}\textsubscript{0} and C\textsubscript{5}\textsubscript{5} have three types of isomers only (meso, CTS, consti.), while C\textsubscript{3}\textsubscript{4} and higher terms possess four (meso of C\textsubscript{3}\textsubscript{4} is 1\textalpha,2\textalpha,3\textbeta,4\beta-1,2-di-hydroxy-3,4-dimethyl cyclobutane). Monoenoic acids are symbolized by a meso isomer of eicosenoic acid [cis-1,2-bis(heptanol)-3-allyl-cyclopropane] and the first term is C\textsubscript{3}\textsubscript{6} (cis-1,2-di-hydroxy-3-allyl cyclopropane). The following isomers are considered consti. isomers of valproic acid (2-propyl pentanoic acid: C\textsubscript{3}H\textsubscript{12}O\textsubscript{2}): 2-ethyl-3-methyl pentanoic acid, di-isopropyl acetic acid, (R)-2-isopropyl pentanoic acid, (S)-2-isopropyl pentanoic acid, octanoic acid [89].

According to our systematics, we have to begin with the finding of a C\textsubscript{3}H\textsubscript{10}O\textsubscript{2} meso isomer. This can be cis-1,2-dihydroxy-1,2-diethyl-3-methyl cyclopropane, cis-1,3-dihydroxy-2,2-diethyl-cyclobutane, \(1\textbeta,2\textbeta,3\textalpha,4\alpha\)-1,2-diethyl-3,4-dihydroxy cyclobutane, or \(1\textbeta,3\textbeta,4\alpha,6\alpha\)-1,3-dihydroxy-4,6-dimethyl-cyclohexane, or others. As can be seen from their structure, the latter three isomers present also CTS and irrechi forms. And the C\textsubscript{3}H\textsubscript{10}O\textsubscript{2} isomers mentioned earlier, valproic acid inclusive, are all consti. (see below). Dienoic acids are made up by the meso isomer of nonadecenoic acid [cis-1,2-bis(6,6'-hydroxy-hexane)-3-butaadienyl-cyclopropane] and the first term is C\textsubscript{7} [cis-1,2-dihydroxy-3-(1-butaadienyl) cyclopropane].

**Epoxides.** We have placed epoxides (Fig. 4) distinctively of alcohols and others since they are in a higher state of oxidation. The two epoxides (cis and trans) have been prepared and separated by chemists in Pennsylvania aiming at drugs intended to alleviate the symptoms of asthma [90]. We have imagined two meso and one irrechi isomers for the two afore mentioned epoxides. Hence the latter are consti. isomers as related to meso ones. The same authors describe three isomers of 1,2-diphenyloxirane (stilbene oxide), one meso and two CTS. Dimethyloxirane is illustrated equivocally [91], although it has four types of isomers: meso, CTS, irrechi, consti. Two enantiomeric geraniol epoxides have been prepared [92], and we have imagined a meso isomer for them (Fig. 4), hence the two enantiomers are consti. isomers.

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**Fig. 3.** Meso isomers of some serial compounds with functional groups

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**Fig. 4.** Meso isomers of some serial compounds with functional groups
2.2 Natural Compounds of Biochemical Interest

A general formula can represent diols, well exemplified by butane diols. As all the other compounds having two asymmetric carbons only, 2,3-butanediol has but a meso isomer and two CTS; 1,3-butanediol is a consti., isomer. Diols can present irrechi isomers only by contribution of alkane chain (see 3,4,5,6-tetra-Me-octane above). Triols, similarly to trimethyl alkanes (see 3,4,5-triMe-heptane) cannot have CTS isomers, but meso, irrechi and consti.; the first term is 2,3,4-pentanetriol. Tetrols presents all four types of isomers, the first term is (2R,3S,4R,5S)-2,3,4,5-hexanetetrol (Fig. 5).

A spectacular example of coexistence in natural materials of consti. and meso isomers in nature can be found in carbohydrate chemistry. Meso-isomers of aldo- and keto-pentoses (C₅H₁₀O₅) are 1,2,3,4,5-pentahydroxy cyclopentanes [93-95]. Aldo- and keto-hexoses (C₆H₁₂O₆) are represented by six meso inositols [31,32] (Fig. 6).
**Fig. 6. Meso isomers of aldoses and ketoses**

**Fig. 7. Meso isomers of the twenty fundamental amino acids. (see also text)**
Biochemical compounds also present meso isomers (Figs. 2-11). Saturated, mono- and polyenoic fatty acids are represented by the isomers of stearic acid, oleic and eicosapentanoic acid (the famous omega-3). As is obvious, an isomer of C_{18}H_{32}O_2 (cis-1,3-dihydroxy-cis-4,6-dihyptl-cyclohexane) presents all four type of isomers: meso (cis-1,3-dihydroxy-cis-4,6-dihyptl-cyclohexane), CTS (as pairs of enantiomers) (trans-1,3-dihydroxy-trans-4,6-dihyptl-cyclohexane, etc.), irechi (cis-1,3-dihydroxy-trans-4,6-dihyptl-cyclohexane, etc.) constitl (stearic acid, etc.). A general formula has been elaborated for mono- and polyunsaturated fatty acids [96].

Compounds with a ubiquitous distribution in living matter, the twenty fundamental amino acids are characterized by an unequaled structural variety. However, without any exception, they present meso isomers (Fig. 7). These amino acids are met especially integrated in proteins and in this state they especially manifest themselves by their tails [85]. Meso, CTS and constit isomers present the following amino acids: Gly, Ala, Val, Thr, Asp, Pro, Phe, Arg, Trp. Meso and constit isomers present the following amino acids: Tyr, His, Ser, Glu, Asn, Gin, Cys, Met, Leu, Ile, Lys and Orn present all four types. Amino acids containing an aromatic fragment and/or a relatively high level of chemical functions are more limited in structural variety. However, we have had again the opportunity to exploit the planar character of benzenoid structures.

For long chain bases (LCB) (sphingosines), LCB d18:1 (Fig. 8) has been selected. Meso isomers have been also found for LCB t16:0, LCB d16:0, LCB d16:1, LCB t18:0, LCB t18:1, LCB t20:0, LCB t20:1. Meso isomers of saturated LCB should use meso isomer of nonanol as a model. Nucleosides, nucleotides and their deoxy counterparts are represented by adenosin and deoxy-adenosin. All prostaglandins have matching meso isomers, as indicated by PGE1, PGF2α, PGE2, PGF3α. All natural and synthetic alkaloids have meso isomers, providing they include a significant alkane moiety e.g. piperidine, piperazine, etc. Camphor is also present. Practically, all hydrosoluble vitamins present meso isomers. A component of coenzyme A, pantoic acid, has pentahydrroxy cyclohexane as a meso pair (Fig. 8).

Squalene presents at least one meso compound. Sterols have been exemplified by cholesterol, stigmasterol, sitosterol, campesterol, ergosterol and digixygenin (Fig. 9). Digixygenin also presents the four types of isomers. A similar solution has been found for estrone, C_{19} (5α-androstanol), C_{21} (prednisolone, 11β-Hydroxy-progesterone, pregnenolone, progesterone, corticosterone, cortisol, aldosterone), C_{24} (biliary acids: cholic, chenodeoxycholic, deoxycholic, lithocholic). All lipophilic vitamins A, D, E, K – present meso isomers (Fig. 10). Vitamin E is represented by α-tocopherol and α-tocotrienol, but all members of this vitamin have meso isomers, and the same are vitamins K1 and K2. Both meso isomers of vitamin K1 and K2 are indicated. The planar structure of benzenoid compounds has been successfully used in meso isomers of the following: biotin (cis-2,4-dihydrxy-3-methyl-3-adenin oxetane), biotin [cis-2,4-dihydrxy-3-propyl-3-(3,4-diamino-thiophene-2)oxetane], adenosin (cis-3,4-dihydrxy-cis-2,5-dihydrxy-1-adenin cyclopentane), FADH_{2}, FMNH_{2}, and even coenzyme A. In order to write meso isomer of FMNH_{2} we extracted an O atom from a keto bond, however leaving redox system intact. An excellent alternative to this is to link the isoalloxazine system and a phosphonic (not phosphoric!) on C-3 of ribitol.

3. TRIANGULAR REPRESENTATION AND MATHEMATICAL EQUATION

A mathematical equation and a triangular representation [96] (Fig. 11) have been imagined to illustrate meso isomers. In equation n-3=2x+2y+z+w, n is the number of chain forming atoms, x, y, z, w are suitably selected numbers. x, y, z, w are connected with R1, R2, R3, R4, respectively. The rings of three or four atoms, as cycles or heterocycles, synthetic [14,97-99] or found in natural materials, are well known. Cis- and trans-1,2-dimethyl cyclopropane are indistinguishable of thermodynamic point of view [100]. 1,2,3-Trihydroxycyclopropane is known as an unstable combination [101,102], however no attempt was made to stabilize it. 1,2-Dihydroxycyclopropane has been prepared by a reduction reaction of a diketone derivatives [103]. Cis-1,2-dihydroxycyclopropane has been discovered in natural material as a glycoside of α-D-galactopyranose [104] as well as in the constitution of mycic acids [105] and lactobacillic acid [85]. Oxirane ring has been identified as (3S)-2,3-oxidosquale in sterols biosynthesis. Two syntheses of cis-1,2,3,4-tetrahydroxy cyclobutane have been reported [106]. Lactobacillic acid can be considered as a model for our paper (Fig. 11).
Fig. 8. *Meso* isomers of some natural compounds, including hydrosoluble vitamins
Fig. 9. *Meso* isomers of some natural sterols

Fig. 10. *Meso* isomers of lipophilic vitamins
AN EXERCISE OF COMPARATIVE CHEMISTRY GIVES AN ANSWER TO AN UNANSWERED QUESTION – WHY IS NATURAL CHEMISTRY AS IT IS?

A question should be raised concerning the hierarchy [47] of the four types of isomers, in other words which of them fills the top place. An intrinsic property of meso combinations is their character of dimerism, hence their molecule is formed of two entities that are contrary in a spatial and optical sense. Of this reason, nine philosophers of ten, probably, should declare meso group as being on the top. We ourselves have selected them as structural reference since we thought they have a higher rank than CTS and irrechi. In fact, meso phenomenon is a distinct and profound philosophical category, totally unexploited by this all-embracing science. Nonetheless, that some people could be fascinated by CTS molecules, since they are produced by doubling of the same entity. If we compare the four types, it’s quite obvious that meso, CTS and even irrechi are characterized by some structural restrictions. Constit., molecules are characterized by fewer such structural restrictions. Of this reason, probably, natural chemistry opted for them.

When physical chemistry appeared and grew stronger, biologists and other scholars connected with biochemistry, optimistically entertained the hope that physical chemists would discover a marker for natural compounds, as density is for gold. Till now such hope never met, according to our knowledge. Nonetheless, natural combinations possess some unique characteristics, and one of them, in our opinion, is the fact that they are less restricted, in structural sense, than meso, CTS and irrechi. A proof for this assertion is the fact that as soon as a living thing dies, nature sends a thousand messengers to recover its component materials.

We reckon that at least one of these characteristics is that constit. compounds have a higher number of freedom degrees, in comparison with the other types. Somehow, this phenomenon is a chemical expression of freedom.

In different classes of compounds which constitute series, a limit has been noticed, and above this limit at least meso isomers are possible, or even all four types. Compounds under this limit have to be considered as archaic. They can reach to the group of combinations able of producing meso isomers only by chemical transformations. E. g. propane belongs to archaic group, however, by oxidation it becomes propanoic acid, an advanced form able to present meso form. Fischer [17,73] illustrated this by preparing a variety C₆ monosaccharides from formaldehyde or C₃ derivatives.

5. CONCLUSIONS

1. Atoms or fragments cut by the mirror plane of symmetry are masked (hidden) of polarized light, and what remains, as evidenced by this physical instrument, is a homodimer.
2. All major natural metabolites possessing a significant alkane moiety and a minimum degree of oxidation have a meso isomer, hence a dimeric matching.
3. Of the four types of isomers – meso, C₂ symmetrical, irrechi, constitutional – nature selected constitutional ones, since they are characterized by the highest number of freedom degrees.
4. A triangular symbol can be imagined, able to represent numerous natural and synthetic compounds, providing the afore mentioned conditions are met.
5. Meso phenomenon discloses a new facet of natural compounds.
COMPETING INTERESTS

Authors have declared that no competing interests exist.

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