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Concept of Absolute Enantioselective Separation

Roman Bielski [a,*], Michal Tencer [b,c,**]

[a] Value Recovery, Inc., 510 Heron Drive, Suite 301, Bridgeport, NJ 08014, USA
[b] University of Ottawa, School of Information Technology and Engineering, Ottawa, 800 King Edward Av., ON, K1N 6N5 Canada
[c] MST Consulting, Ottawa, ON, Canada

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ABSTRACT

A novel approach to separations of racemates is described. It is a chromatography-like process in which molecules to be separated are oriented in two directions perpendicular to each other and parallel to the surface. If this requirement is met the opposite enantiomers differ in the energy of interaction with the surface. We call the process Absolute Enantioselective Separation (AES). Surface requirements for resolving a racemate to enantiomers are discussed. AES can be accomplished either by interaction of racemate components with a repeating pattern on the not necessarily chiral surface and interaction with a static electric field or by interaction with two repeating patterns defining the chirality of the surface. Additionally, a multiple use of electric fields to enable a separation in bulk is described. The ease of separation of selected natural compounds (amino acids and monosaccharides) in the AES process is also discussed.

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1. Introduction

1.1. Absolute asymmetric synthesis (AAS)

Asymmetric synthesis is defined as stereoselective synthesis of chiral compounds [1]. In principle, it requires that a chiral influence is employed. Usually, this influence is of chemical nature, *i.e.* there is an enantiopure compound involved. This enantiopure compound can contain additionally a prochiral center that is transformed into a chiral one. Another possibility is that the prochiral center to be transformed to a chiral one and the enantiomerically pure center (acting as a reactant, solvent or catalyst) are present in different compounds [2]. Thus, the advantage is taken of the fact that corresponding diastereoisomers differ in their physical properties and, for example, can be separated. A more challenging task is an *absolute asymmetric synthesis* (AAS), *i.e.* "the formation of enantiomerically enriched products from achiral precursors without intervention of chiral chemical reagents or catalysts" [3]. Typically, AAS requires the use of a physical chiral influence such as circularly polarized light [4], a static magnetic field collinear with light (not necessarily polarized) [5,6] or interaction with chiral crystals of non-chiral compounds [7]. The number of useful chiral influences is rather limited [8,9], and thus, there has been a constant search for new ones.

A set of three orthogonal vectors is chiral. Let us consider such a set ($\mathbf{x_1}$, $\mathbf{y_1}$, $\mathbf{z_1}$) (Fig. 1). For clarity we will make these vectors parallel to the Cartesian axes *X*, *Y* and *Z*. Let us add a plane *P* which intersects the *X* and *Y* axes and let this plane be a mirror. Reflecting ($\mathbf{x_1}$, $\mathbf{y_1}$, $\mathbf{z_1}$) in the mirror results in the set ($\mathbf{x_2}$, $\mathbf{y_2}$, $\mathbf{z_2}$) where $\mathbf{z_2} = -\mathbf{z_1}$ which is not identical (super-imposable) with the original set as shown in Fig. 1, and therefore, it is by definition chiral.

The fact that a set of three vectors perpendicular to each other is chiral was known already by Immanuel Kant [10]. The question arises whether this fact can be taken advantage of when performing an absolute asymmetric synthesis (AAS). In other words, can a set of three perpendicular vectors[1] serve as a chiral influence?

Let us consider a molecule of a prochiral compound **1** (Fig. 2a) [11]. Due to the action of the orienting factor represented by the vector **E** the molecule is oriented along the *Y* axis (for example, let **E** represent an electric field and let the carbonyl group in **1** be responsible for its dipole moment). Another orienting force **G** additionally orients the molecule **1** along the *Z* axis (for example, as a result of interaction with the surface *P* as shown).

* Corresponding author. Tel.: +1 610 967 9754; fax: +1 856 467 6317.
** Corresponding author at: University of Ottawa, School of Information Technology and Engineering, Ottawa, 800 King Edward Av., ON, K1N 6N5 Canada. Tel.: +1 613 562 5800x2176.
E-mail addresses: bielski@ptcvalue.com, bielski1@verizon.net (R. Bielski), michaltencer@hotmail.com (M. Tencer).

[1] While the vectors do not have to be perpendicular the effect of their action is the strongest when they are. The effect will be zero only if some angles between two of those vectors are zero. For brevity we will use the word orthogonal or perpendicular but it should be understood that the angle between vectors can be smaller.

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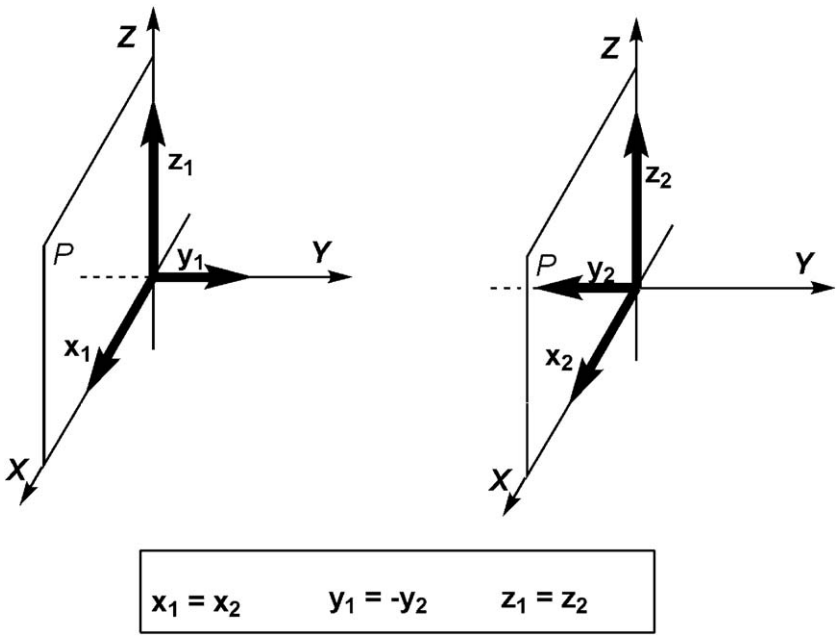

Fig. 1. A set of three orthogonal vectors is chiral.

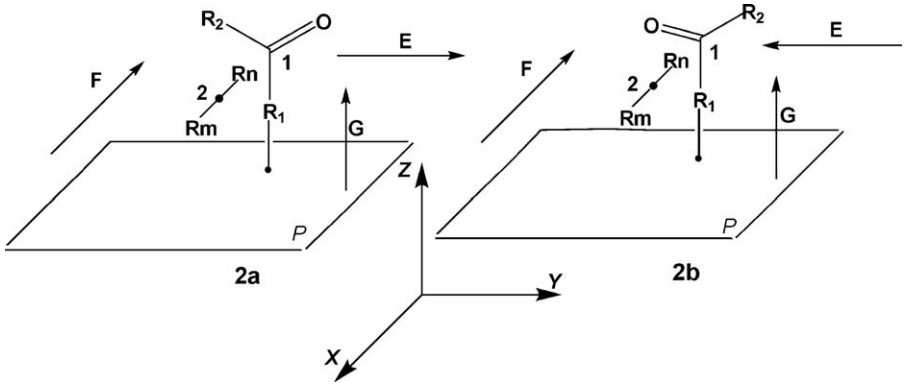

Fig. 2. (a and b) Visual representation of a reaction taking place between oriented reactants.

Now, let us assume that the molecule of a second reactant **2** is oriented by a third orienting factor **F** along the third axis (*X*). Let Rn be a nucleophilic end of the molecule. Then the resulting product will be chiral and the absolute configuration of the prevailing enantiomer can be always predicted. In thus described process:

- The enantiomeric excess of the product depends only on the degree of the orientation of reactants, the described methodology is different from the one employed by catalysts such as enzymes. Enzymes achieve very high stereoselectivity by enforcing the mutual orientation of reactants molecule by molecule. After the reaction is complete the products leave and the next set of reactant molecules enter the active sites of the enzyme and the process is repeated. In the process discussed here the mutual orientation of reactants is enforced in bulk, *i.e.* all the molecules are oriented in space and versus each other. In other words in the proposed approach the introduced chirality is macroscopic while with the former case it is of microscopic (a better word would be nanoscopic) nature. In the future it will be very interesting to look at kinetics of reactions in which the reactants are so mutually oriented.
- The picture shown in Fig. 2b differs from 2a only in the sense of the vector **E**. If **E** is a vector representing the action of a static electric field it would be an equivalent of changing the sense of the electric field. The absolute configuration of the product formed in excess will be different in both cases shown.

1.2. Implementation of Absolute Asymmetric Synthesis in the presence of orienting fields

A scheme proposed to implement AAS [11] is shown in Fig. 3. Since there are not many useful orienting factors, we will apply a static electric field twice. The flat surface **3** equipped with hydroxyl groups can be reacted in the presence of a strong electric field with the dibromo-compound **4** to produce the ether **5**. The purpose of the dialkylamino and trifluoromethyl groups in the compound **4** is to introduce a prominent dipole moment. After the formation of two covalent bonds with the surface the spatial orientation of **5** is frozen and the electric field can be removed. Next, the reaction with methyl iodide forms the product **6** containing no free hydroxyl groups. Now, **6** is reacted with a metal-organic compound **7** in the presence of the electric field this time turned by 90°. The R group can be an alkyl group and Z represents a metal such as lithium, magnesium or zinc. The reaction at the carbonyl center will afford (after the hydrolysis and hydrogenation) the final product **8**. If R = CH_3 the absolute configuration of the dominant enantiomer will be R.

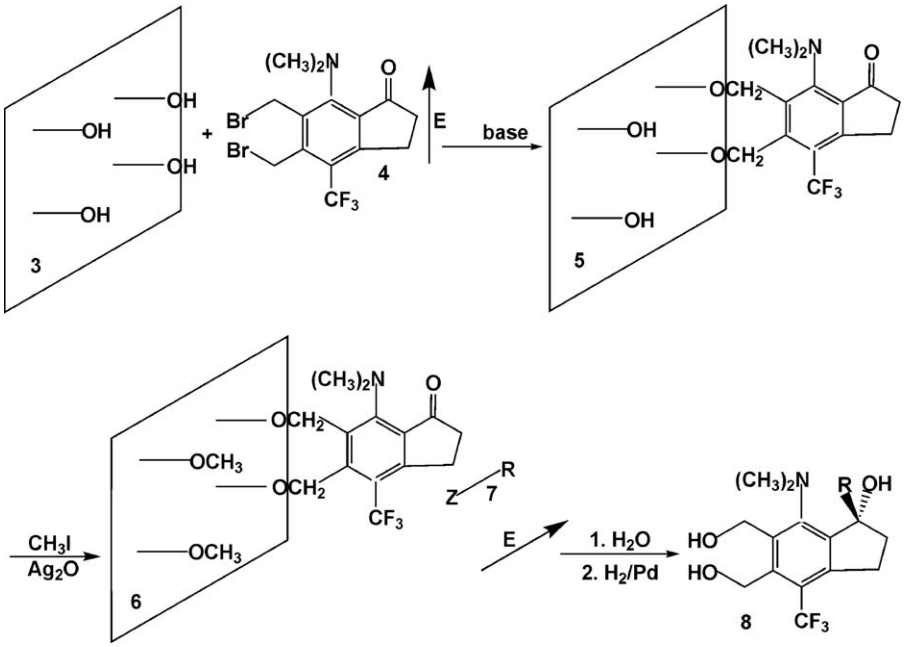

Fig. 3. A possible execution of the AAS in the presence of three orienting forces (reproduced with permission from Ref. [11]; copyright by NRC Research Press 2003).

After our paper describing the AAS [11] appeared, Professor Kagan [12] pointed to us a related set of papers from the early eighties. Robinson and Holland [13–15] published elegant studies in which the mutual orientation of reactants was accomplished by using one surface of an appropriate single (non-chiral) crystal as a chiral template. First, large single crystals of tiglic acid **9** grown from acetone were embedded in an epoxy resin. Next, a single crystal was cut into two portions exposing the two chiral surfaces of opposite handedness. Finally, the accessible surfaces were subjected to oxidation with osmium tetraoxide as shown in (simplified) Fig. 4. The control experiment has shown that cis-hydroxylation products diffuse relatively rapidly from the surface of the crystal, *i.e.* the reaction takes place mainly on the surface. The accomplished enantiomeric excesses in this and other similar additions to the double bond were up to 33%. In this case of the three orienting factors one is due to the presence of the surface and the other two are related to the orientation of molecules within the specific crystal structure. Recently, Kuhn and Fischer [16] expanded the scope of the approach to reduction with $NaBH_4$.

2. Absolute Enantioselective Separation (AES)

2.1. The process

Let us consider an enantiomer **11a** shown in Fig. 5a which is spatially oriented by factors **E**, **F**, **G**. Due to **F** the substituent R_4 is

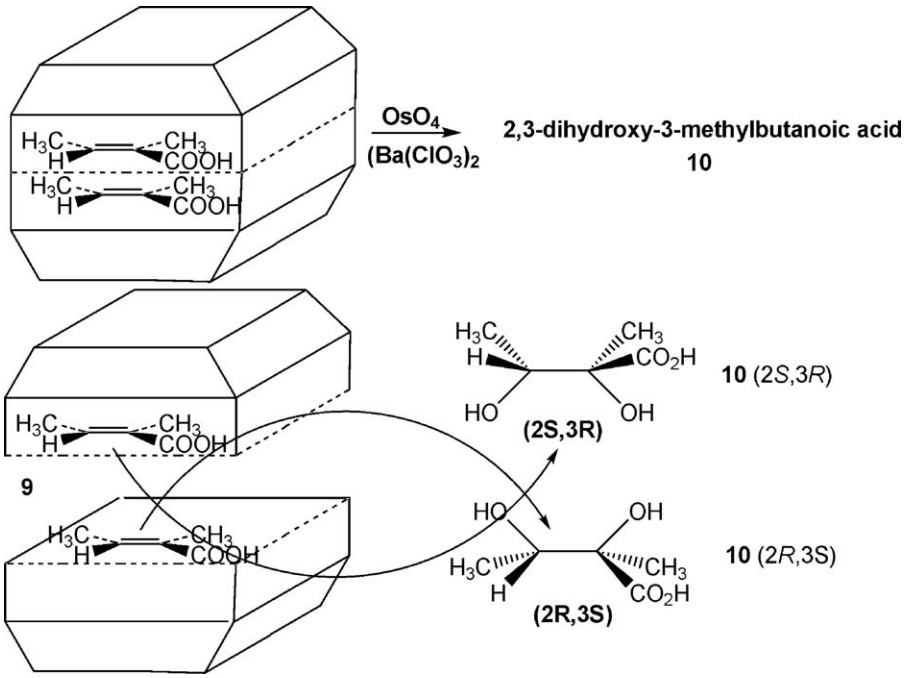

Fig. 4. The reaction of tiglic acid **9** with osmium tetraoxide (reproduced with permission from Ref. [34]; copyright by Bentham Science Publishers 2008).

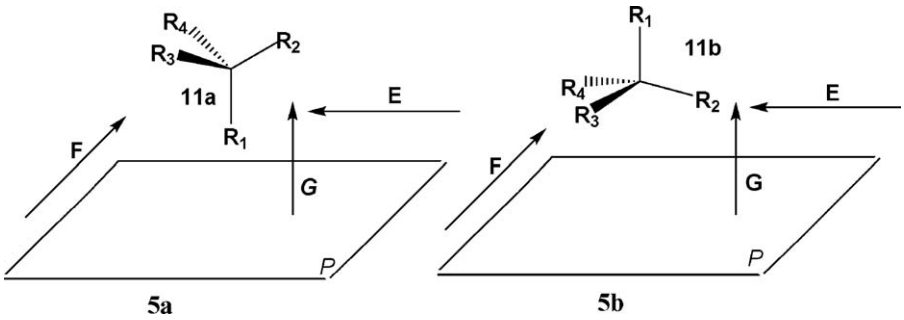

Fig. 5. (a and b) R and S enantiomers oriented by the same set of factors and the surface.

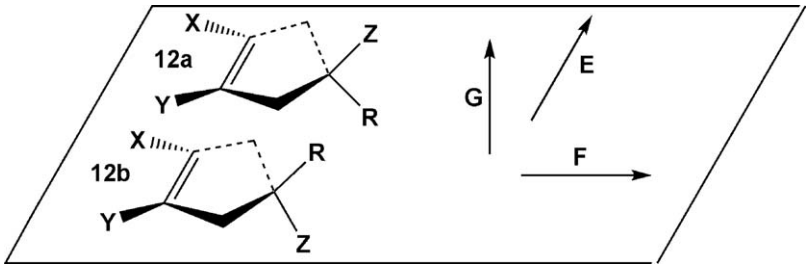

Fig. 6. Field-oriented enantiomers of a cyclopentene derivative and the surface (reproduced with permission from Ref. [29]; copyright by Springer 2007).

further from us while the substituent R_3 is closer to us (as shown). Additionally, due to **E** the substituent R_2 is on the right-hand side of Fig. 5a, and thus, the substituents R_3 and R_4 are on the left-hand side. The result of this orientation is that the substituent R_1 is directed towards the surface provided it is located below the molecule.

Fig. 5b shows the opposite enantiomer **11b**. Let us assume that again the force **F** causes that the substituent R_4 is further from us while the substituent R_3 is closer to us. Let the action of the force **E** causes that the substituent R_2 is on the right-hand side and the substituents R_3 and R_4 are located on the left-hand side. As it can be seen, the substituent R_1 is directed either away or towards the surface P.

The conclusion is very clear: *if a racemate at a surface is subjected to two orienting factors which are parallel to the surface but perpendicular to each other, the energy of interaction of opposite enantiomers with the surface will* **not** *be the same*. We should be able to take advantage of this fact and resolve the racemate by moving the enantiomers along the surface like in chromatography. In such a process at each "theoretical shelf" the partition of the enantiomers between the solvent and the surface will be different, thus they will move with different rates. We call the process Absolute Enantioselective Separation (AES) [17] to highlight the fact that it uses no chiral chemicals with the exception of those that are being separated.

Recently, a novel phenomenon of compositional disproportionation taking place during chromatography of enantio-enriched compounds, especially ones having trifluoromethyl groups, on achiral stationary phase has been discovered [18–21]. This fascinating process bears a superficial similarity to AES. However, while the latter depends on differential interactions with the surface, with the former the source of the enantiomeric enrichment is formation of homo and heterochiral dimers or other oligomers with different properties. Thus, the observed disproportionation is not limited to chromatography and may be also observed in other circumstances. Although based on a different type of interactions, both processes may lead to optically pure compound starting with a mixture of enantiomers [18–21].

2.2. Simultaneous separation of enantiomers and diastereoisomers

Let us consider another pair of enantiomers represented by **12a** and **12b** (Fig. 6). The enantiomers are oriented by the factor **D** so that the substituents Z and R are prevalently located on the right-hand side while X and Y are located on the left-hand side. Furthermore, in both enantiomers X is further away from the viewer than Y due to the action of the orienting factor **E**. This can be achieved, if X and Y introduce a large dipole moment into the cyclopentene ring and **E** is electric field. It is clear that the energy of interaction of enantiomers **12a** and **12b** with the surface is different because in the former case the R group is interacting with the surface while in the latter the Z group is directed towards the surface.

Now, let us consider a separation of a mixture shown in Fig. 7. The relation between the pair of enantiomers **13a** and **13b** and the other pair of enantiomers **14a** and **14b** is diastereoisomeric. As before, all the components of the mixture are oriented by the factors represented by vectors **E** and **F** so that Y is further from the viewer than X and Zs are on the right-hand side. Let us limit the interaction of the separated molecules with the surface to formation of hydrogen bonds. Enantiomer **13a** has two hydroxyl groups directed towards the surface. Since enantiomer **13b** has no such hydroxyl groups we expect the energy of interactions between **13b** and the surface to be significantly smaller than that of the enantiomer **13a.** Thus, **13b** should move faster than **13a** in AES process. The second pair of enantiomers (**14a** and **14b**) have only one hydroxyl group directed towards the surface so we expect their Rfs to be closer to each other but different from those of **13a** and **13b**, having in fact, immediate values. Thus, the AES process is capable of separating not only enantiomers but diastereoisomers as well. It is important when discussing the pre-biotic origin of biologically important enantiopure compounds. There are many known cases of opposite enantiomers exhibiting different energy of interaction with chiral surfaces [22–25].

2.3. Orienting molecules to be separated

How can the molecules to be separated in the AES process be oriented in three orthogonal directions? There is a number of

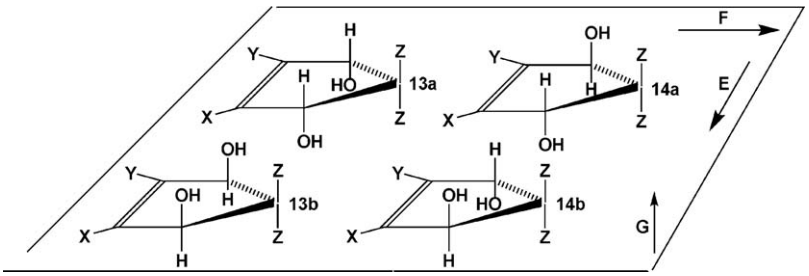

Fig. 7. Separation of enantiomers and diastereoisomers (reproduced with permission from Ref. [33]; copyright by Springer 2007).

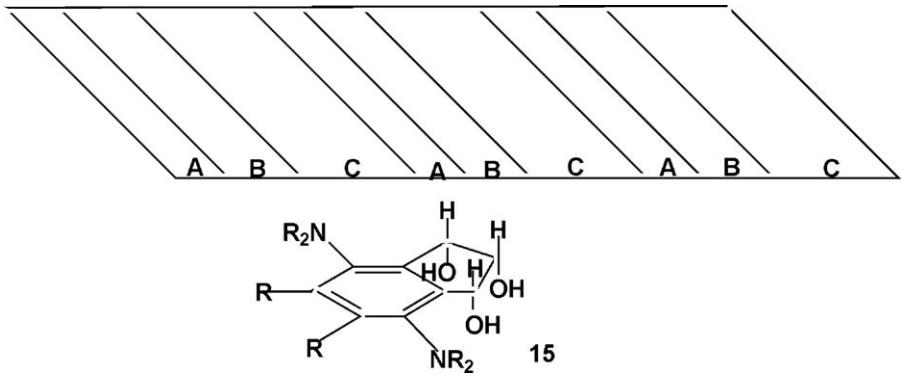

Fig. 8. A repeating pattern on the surface orienting molecules in one direction.

possible mechanisms supplying three orthogonal directionalities to the system thus enabling AES. Such mechanisms can be different combinations of: the presence of a surface, one or more actions of electric field or other physical fields and monodirectional or bidirectional patterns on a surface (natural or designed). Notable combinations of these factors include:

1. A bulk (“monolithic”) stationary phase [22,26], typically a polymer which is given a permanent orientation in two directions by, *e.g.*, static electric field applied twice at 90°, each application being followed by polymerization or cross-linking while the molecules of the racemate to be resolved are oriented by the electric field in the third direction.
2. Orientation by electric field parallel to the surface + interaction with a repeating pattern on the (flat) surface.
3. Interaction with two orthogonal repeating patterns on the surface. This is equivalent to a chiral surface, here however, we are interested in “designer” surfaces matching a certain type of molecules, *e.g.* sugars and we will discuss this case in more detail.

In the two last cases one direction (orthogonal to the surface) is defined by the presence of the surface.

Let us examine how molecules can be oriented due to an interaction with a repeating pattern on the surface (case 2). As illustrated in Fig. 8 a molecule **15** consists of three regions: a hydrophobic one represented by substituents R, a hydrophilic one containing the dialkylamino substituents NR_2 capable of forming hydrogen bonds with appropriate functionalities (*e.g.* OH or NH on the surface) and the third region equipped with hydroxyl groups capable of forming hydrogen bonds with free electron pairs of such atoms as fluorine or nitrogen. Now, if the domains A, B, and C on the surface are equipped with such necessary functional groups and the distances between parallel lines representing domain limits fit the appropriate molecule fragments, then the molecule **15** will be oriented. Even when moving due to the movement of the solvent it will be oriented mostly with the hydroxyl groups directed towards the domain C (to the right) and R groups directed mostly towards the domain A (to the left).

We will show that a chiral surface can orient molecules also in two directions. Let there be on the surface periodically repeated functionalities X, Y and Z. These functionalities can be considered as vertices of triangles with a twofold translational symmetry as shown in Fig. 9 [23,27].

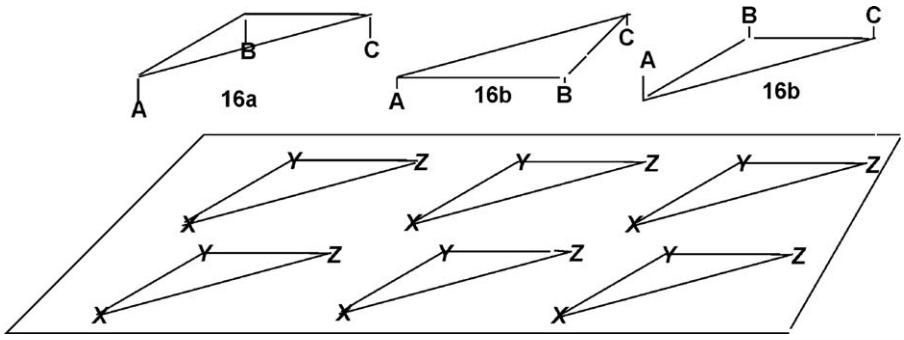

Fig. 9. Interaction of an enantiomer with a pattern on the surface leading to orientation in two directions.

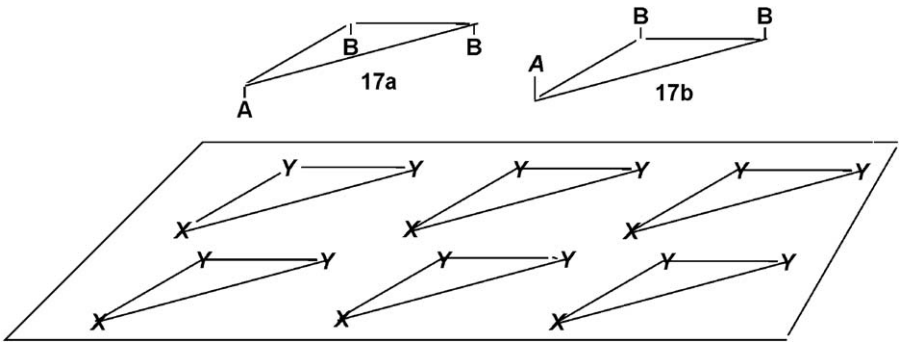

Fig. 10. Simpler interaction of an enantiomer with the pattern on the surface leading to orientation in two directions.

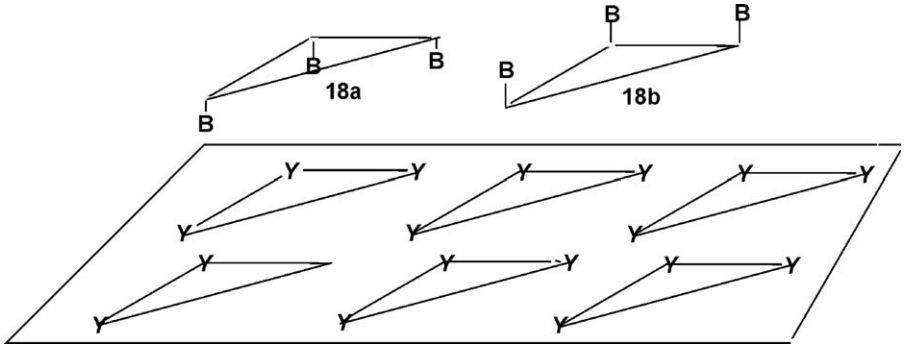

Fig. 11. Scalene triangles on the surface are chiral and all substituents in **18** can be the same (easy in geometry but difficult in chemistry).

Now, let us assume that substituents A, B and C of the chiral compound **16** form strong interactions with X, Y and Z, respectively. It is clear that the enantiomer **16a** fits perfectly into the (chiral) surface while the opposite enantiomer does not. Thus, we will expect **16a** to move slower than **16b** which can have no more than two substituents interacting with the surface at a time. At this moment **16** is only a hypothetical structure.

The geometrical requirements for the enantioselective molecule-surface interactions can be even simpler as shown in Figs. 10 and 11. All these figures (Figs. 9–11) clearly show that the two-directional orientation of molecules on the surface requires at least three points of interaction with the surface which is an equivalent of two orthogonal vectors.

One possibility of having chiral surfaces derives from the chirality of the appropriate crystals. A substance does not have to be chiral to form chiral crystals (*e.g.* quartz). On the other hand, surfaces of chiral crystals must be chiral [7,24,25,28,29]. Fig. 12 shows how a chemically modified, racemic, α-*D*,*L*-ribopyranose could be separated in the AES process on the appropriately designed chiral surface (R can be here methyl groups). Hexagons on the surface do not necessarily describe actual chemical structures, their purpose being only to highlight the surface geometry that would fit into the structure of the *D*-enantiomer (**19D**) but not into the structure of the *L*-enantiomer (**19L**).

Another type of chiral surface suitable for the AES process is formed when prochiral molecules are adsorbed on a non-chiral surface [25,30–32]. For example, Fig. 13 shows a picture of left-handed and right-handed domains obtained when a purine base, adenine formed monolayers on the surface of a non-chiral mineral, molybdenite (MoS_2) [30].

2.4. AES of monosaccharides

Let us look now at the resolution of some natural products in the AES [33,34]. It seems that the AES process can be facilitated by the increased number of chiral centers, particularly when they are in the ring. Hence, we can predict that racemic monosaccharides will be easier to separate to enantiomers than racemic amino acids

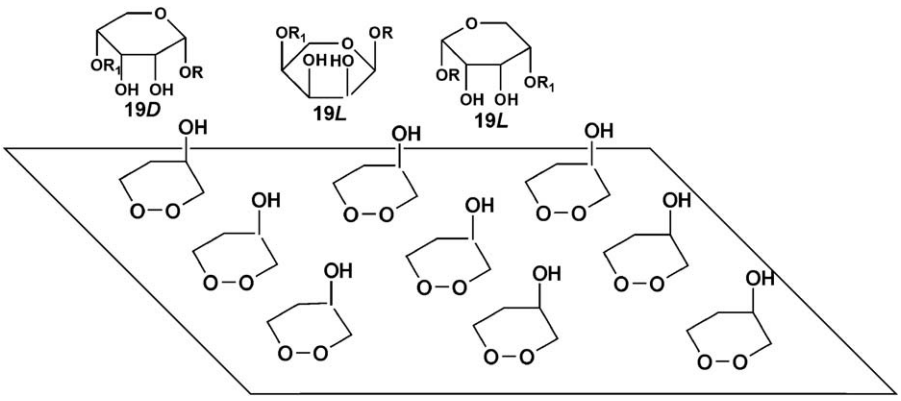

Fig. 12. The AES of a derivative of α-*D*,*L*-ribopyranose on a chiral surface.

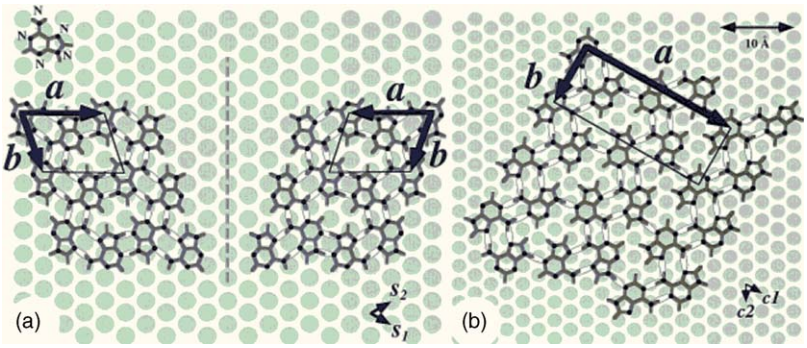

Fig. 13. (a and b) Adenine on the surface of molybdenite (reproduced with permission from Ref. [30]; copyright by Springer 1996).

since natural amino acids comprise only one or two chiral centers. Perhaps, that is why nucleic acids contain a carbohydrate and not an amino acid as the chiral unit.

Let us also compare various monosaccharides in the AES. It seems advantageous for the sugar ring to be more or less parallel to the surface. Within furanoses (sugar hemiacetals or acetals forming 5-membered ring) the largest difference in interaction with the surface will be expected for the components of α-*DL*-erythrofuranose (shown in the Haworth projection – Fig. 14). If both enantiomers are oriented in the same way they will have all the three hydroxyl groups (including the anomeric one) directed either towards or away from the surface.

The effect should be even stronger for racemic α-ribopyranose (**21D** + **21L**) where opposite enantiomers will have as many as four hydroxyl groups directed either towards or away from the surface (Fig. 15). Racemic α-*DL*-ribopyranose seems to be a racemate easier to separate to enantiomers in the AES process than any other monosaccharide. It is because both ketoses and aldoses of higher monosaccharides (hexoses, heptoses, *etc.*) must have at least one or two carbon units sticking out of the ring. The conclusion will not be affected by any modification of carbohydrates provided that the same substitution applies to all the compared carbohydrates.

Sugars capable of forming cyclic hemiacetals can exist in solution as a mixture of α- and β-furanose plus α- and β-pyranose forms and the open form. Ribose in aqueous solution is a mixture of all possible forms. In the presence of borate ions the furanose form is prevalent [35]. Nevertheless, α-ribopyranose is expected to be a dominant form interacting with the surface because it has four hydroxyl groups on one side of the pyranose ring. Incidentally, for the same reason of all natural monosaccharides ribose is expected to be one of the most strongly adsorbed on the surface. Non-substituted carbohydrates have rarely been chromatographed in a non-reversed phase system. Nevertheless, there are a few reports [33,36] showing that ribose is indeed the slowest (or one of the slowest) monosaccharides when unmodified (non-substituted) sugars are separated using a normal phase chromatography.

So far we assumed that adsorption takes place mainly due to the formation of hydrogen bonds. However, carbohydrates are known to form strong complexes with metal ions in solution. These complexes are particularly strong when metal cations are calcium or lanthanides and sugars are capable of the formation of axial-equatorial-axial positions of three adjacent hydroxyl groups [37,38]. Ribose is one of a few monosaccharides belonging to this category. Angyal [37] states that the stability constant of a complex of α-*D*-ribopyranose with calcium ion is larger than that of other aldopyranoses with the exception of α-*D*-allopyranose. "Sugars common in Nature, with the exception of *D*-ribose, do not complex readily"[37]. Fig. 16 shows the structure of the crystalline complex formed between praseodymium chloride and *D*-ribose [39].

In the light of the above discussion we can offer the following scenario describing the formation of enantiopure compounds some 35 hundred million years ago [33].

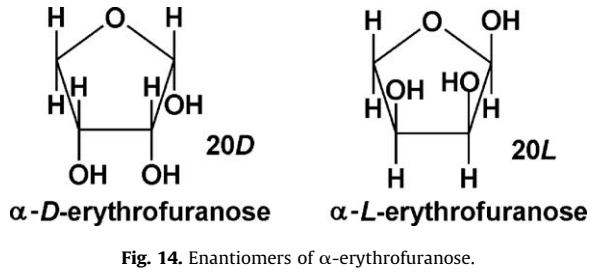

Fig. 14. Enantiomers of α-erythrofuranose.

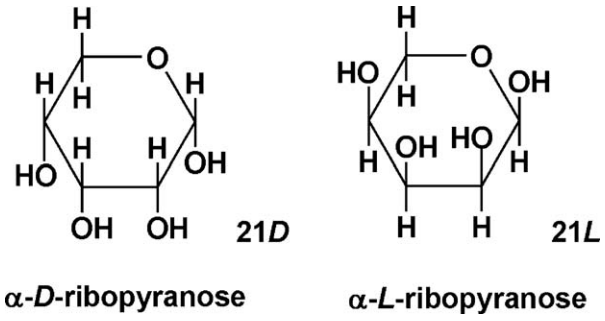

Fig. 15. Enantiomers of α-ribopyranose.

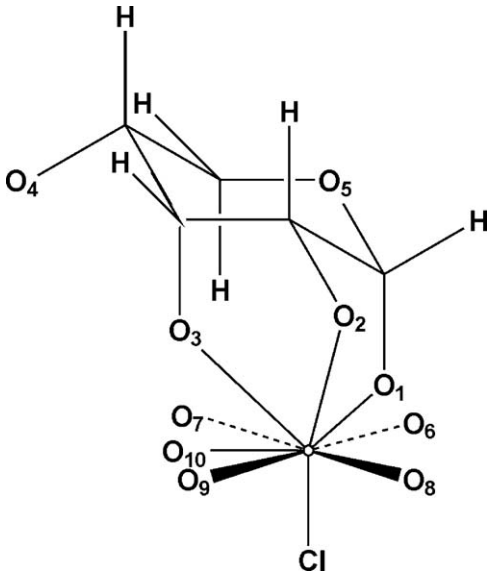

Fig. 16. The geometry of the complex $PrCl_3 \cdot \alpha$-*D*-ribopyranose$\cdot 5H_2O$.

First, the formose reaction took place. It is a reaction of formaldehyde in the presence of a base such as calcium hydroxide [40]. It could have been the Eschenmoser version which produces a relatively simple mixture with ribose being one of the main products [41]. Next, the mixture could have been modified to introduce specific functionalities into the same position of all the monosaccharides formed. Then, this mixture was subjected to the AES process. One of the monosaccharides moved slower on the chiral surface than other mixture components (a ribose enantiomer, other pentoses, other sugars) and, thus, was isolated from the mix. It happened to be α-*D*-ribopyranose **21D**. If the "column" was sufficiently long the resolution could have produced not only the enantiomerically enriched but even enantiopure compound. Thus, no chiral amplification would be needed to achieve pre-biotic homochirality. Such pure product could have persisted in a stable crystalline form for a long period of time. When the appropriate conditions developed in the environment it would have reacted to form nucleosides, nucleotides and, eventually, nucleic acids. The RNA world is consequence of such a scenario.

We think that this scenario not only explains the origin of enantiopure compounds (homochirality) but also gives a plausible answer to the question "why ribose?", *i.e.* why this particular sugar rather than another one is a component of nucleic acids. It is likely that ribose was the only racemate formed in the formose-like reaction which Nature could resolve using the AES process.

3. Conclusion

Absolute Enantioselective Separation (AES) is a process in which a racemate is resolved without intervention of chiral molecules. The crucial to the success of the AES is different orientation of opposite enantiomers against the stationary phase. The concept offers a plausible explanation of the origin of homochirality, and therefore, is important to the hypotheses of life's origin. Equally important may be the applied aspect of AES. At this point, it appears feasible to resolve a racemate using available chiral surfaces and this will be pursued experimentally. The biggest promise as well the biggest challenge will be to design and built custom made surfaces for specific separations, most likely with the help of rapidly progressing nanofabrication techniques. There is no doubt that due to extreme properties of fluorine (electronegativity, electron affinity, *etc.*) its chemistry will be a big part of this effort.

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