CHIRAL VERSUS CHEMICAL EVOLUTIONS AND THE APPEARANCE OF LIFE

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ABSTRACT

The need is emphasized for a common investigation of chemical and configurational evolutions with regard to the major chiral biomolecules as a whole and some experimental lines are developed.

INTRODUCTION

The present state of investigation on molecular and biological evolutions brings out the existence of a sort of "wall" or "black box" of knowledges separating them. This barrier includes different processes such as replication, translation, membrane formation, etc. which probably appeared stepwise in a relatively short period of time. These steps are becoming better and better understood from a prebiotic point of view. However the incidence of optical activity, a feature so tightly bound to present life, is frequently ignored although it is clearly a part of the "wall" (Figure 1).

Indeed, there are no reasons why the chiral elements in the first living organisms should have an optical activity much reduced as compared to the present state. A so-called "racemic" life is difficult to conceive.

Reciprocally, the idea that optical purity may have spread over the surface of the earth before appearance of life does not seem tenable. The chiral forces that may have been acting have very weak effects. Any excess of one enantiomer (arising either by fluctuations or by chiral environment), eventually amplified for instance by broken symmetry processes, can only have led to local and tempo-

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rary concentrations of optically pure compounds, exposed to diffusion and/or spontaneous racemisation reactions that tended to increase entropy again.

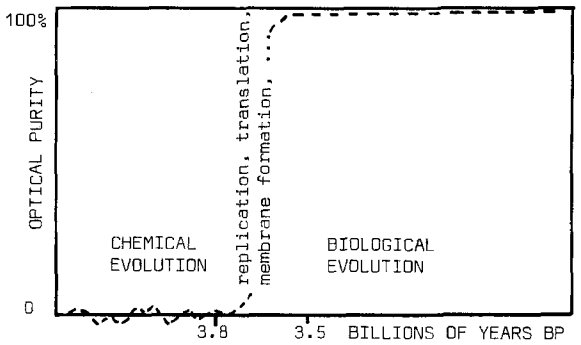

Figure 1. During chemical evolution local and temporary fluctuations of optical activity may have occured whereas almost full optical purity is reached in animate matter.

Thus, there is a need for an approach taking into account together the chiral and the chemical (functional) evolutions, eventually at each step of the barrier, and for the whole of the relevant biomolecules (1). Such an approach should strengthen the most plausible pathways of evolution, or at least allow to rule out the inconsistent ones, and conversely it can suggest new experiments.

CHIRALITY AND PRESENT LIFE

While approaching the problem one should keep in mind some characteristic features of present life.

i. Nature has selected among different possibilities a combination of chiral molecules, aminoacids belonging to the L configuration, nucleotide sugars to the D, phosphatidic acids to the 3-L one. This choice must be the result of subtle interactions that exist at the molecular or macromolecular levels. It is certainly not fortuitous (although the mirror set may have been equally probable, calling chance what we cannot presently better define). Thus the choice of another set, say L-aminoacids, L-sugars together with 3-L-phosphatidic acid, has been avoided.

ii. Present life occurs in small volumes or cells enclosed by membranes themselves built up with chiral molecules providing an asymmetric envelope.

iii. Some of the major biomolecules bear to-day more than one asymmetric center, i.e. two for some aminoacids, three or four for

the nucleotide sugars, two or more for certain lipids either in the polar head or in the fatty moiety. This increases dramatically the number of possible stereoisomers and it may well be that in earlier time the situation was less drastic.

iv. There are substances which are not often taken into consideration in evolutionary schemes. These are coenzymes or vitamins that display also interesting configurational properties, particularly those deriving from isopentyl (isoprenoid) oligomers (Figure 2).

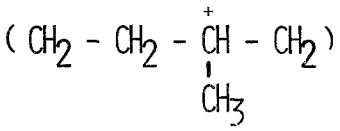

Figure 2. Isopentyl motif with a chiral (+) carbon atom.

They bear a stereoregular backbone like synthetic polymers that can in principle be obtained abiotically with inorganic stereospecific catalysts.

PROPOSALS

The considerations just mentioned suggest some proposals that can possibly be approached by theoretical or experimental chemistry.

i. It may be fruitful to seek for the significance of remnant D-aminoacids or L-sugars, considered as vestiges, found for instance in cell walls or in antibiotic molecules.

ii. With regard to the stereospecific interactions, it may be worthwhile to search for the rules that allowed the choice of the above-mentioned set of chiral bioelements (aminoacids, sugars, lipids, isopentyl motif), either in covalent or non covalent compounds, including dynamic processes. For instance, stereocoselection could be looked for in crystallization, polymerization, etc..

One may also ask e.g. wether aminoacyl nucleotide anhydrides are more easily formed between a desoxy D-ribose nucleotide triphosphate and an L- or a D-aminoacid.

Likewise, examination of atomic models reveals that in a 3'-nucleotide aminoacid ester the asymmetric carbon atoms of the aminoacid (Cα) and of the nucleotide sugar (C-3' and C-4') are brought in close vicinity by ammonium-phosphate electrostatic interactions (Figure 3). This may be a favorable situation for the costereoselection of L-aminoacids and D-ribose or desoxyribose.

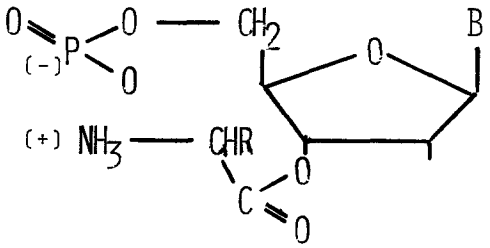

Figure 3. 3'-nucleotide aminoacid ester

In the same way, interactions between chiral lipids and other biocomponents may reveal meaningful results. It has been found that D- and L-alanine are differently ordered on a membrane model system of decyl-2 sulfate (2). It seems however that present phospholipid molecules are not able to recognize the chirality of a neighbour molecule. Their asymmetric center is in some way buried in a voluminous polar head (3). Still, the idea first expressed by Arnett in 1981 (4) that two-dimensional resolution of chiral lipids may open a new explanation for stereoselection appears very attracting. This indeed could lead to the formation of vesicles with an asymmetric envelope sieving inside the volume other chiral molecules able to make for instance stereospecific catalysts. Should this hypothesis be valid, than the chirality of earlier lipids must have play an important role and membrane formation must have taken place in a rather early period of the "black box" evolution. Of interest are other lipids bearing asymmetric centers in the fatty moiety such as the tetraisopentyl fatty alcohol radical of *halobacterium cutirubrum* lipid, or lipids with a less hindered polar head.

iii. If chiral simplicity was initially important, than one can assume that some nucleic acid ancestors were configurationally less complex than the present ones. These ancestors could include only one significant asymmetric center per monomeric unit, such as found in an isotactic polyglycerol phosphate ester. Nature still affords such a backbone in the cell wall teichoic acids (Figure 4). Possibly the difficulties encountered in the abiotic synthesis of nucleotides result in part from the chiral complexity of ribose.

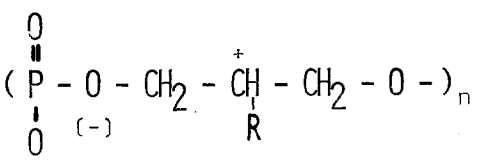

Figure 4. Structure of the teichoic acids. R = sugar or D-amino-acid. With R = CH_2-base: simplified model for nucleic acids. (+): chiral carbon atom.

Polyglycerol phosphate esters substituted with a base may well pair in complementary double stranded helices. This chiral secondary stucture may allow stereoselective reactions, leading for instance to ribose, or specific interactions with peptides. Synthesis run in our laboratory can afford an answer to this question.

CONCLUSION

The aim of this paper was to stress the need for a joint examination of chiral and functional evolutions of the whole of the biomolecules as a mean to discard the less plausible pathways through the frontier between inanimate and animate matters, and to suggest new experiments, some of which are described.

It is interesting to notice that while doing this examination, a certain convergence appeared: the chiral isopentyl motif is found in lipids and cofactors, phosphate esters of glycerol are found in lipid molecules as well as in teichoic acids taken as model for ancestral nucleic acids. This may not be just a coincidence.

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