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MOLECULAR TAPHONOMY OF MEMBRANE CONSTITUENTS. THE SEARCH FOR THE MOST PRIMITIVE MEMBRANES.

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Taphonomy is the study of fossilization processes, and includes "reconstruction" of past animals from their fossils. At the molecular level, the study of the organic constituents of sediments (crude oils and coals, but also clays, shales, etc) has yielded hundreds of structures, essentially in the hands of P.Albrecht and his co-workers in Strasbourg. These are sometimes hardly modified molecular fossils of known natural products. For instance, cholestane "must" come from cholesterol : reductions are frequent molecular taphonomic processes. Diacholestane, also frequently present in sediments, might be derived from "diasterol", an unknown but biosynthetically reasonable rearranged cholesterol ; however, the ease of rearrangement of cholesterol to diasterane derivatives by moderate heating with clays suggests rather that diacholestane derives also from cholesterol ; Wagner-Meerwein rearrangements are reasonable taphonomic processes.
To interpret data from organic geochemistry, one must therefore collect trustworthy precise structural data, rely on the extensive catalogs of natural products structures and of biosynthetic process, and know which molecular taphonomic processes are plausible.
Known molecular fossils belong to several natural products families, including porphyrins obviously derived from bacterial pigments ; by far most of them are derived from terpenoid precursors, as expected as biodegradation of highly branched structures is notoriously difficult. It was also not unexpected to find, frequently, molecular fossils of some archæal lipids : phytane and pristane, which could also have come from chlorophyll or from tocopherols, but also bisphytane, the structure of which became meaningful only once the C_{40} chains of phospholipid ethers of thermophilic and of methanogenic archæa became known.
In other cases, while the structures of the precursors could be derived without doubt, they did not tally with any known one. The most spectacular case of these "orphan fossils" has been that of the ubiquitous geohopanoids, triterpene derivatives carrying an additional n-C_5 chain, for which more than 250 structures have been fully demonstrated ; their ubiquity and abundance in sediments make them probably the most abundant natural products on Earth ! Their precursors, the bacterial hopanoids, were discovered initially in two particular bacteria, but later, by M.Rohmer, in many very varied bacteria , with very varied structures (more than 40 established so far, including the fantastic adenosylhopane).
Based on the molecular dimensions and amphiphilic character of bacterial hopanoids, we postulated that they reinforce bacterial membranes like

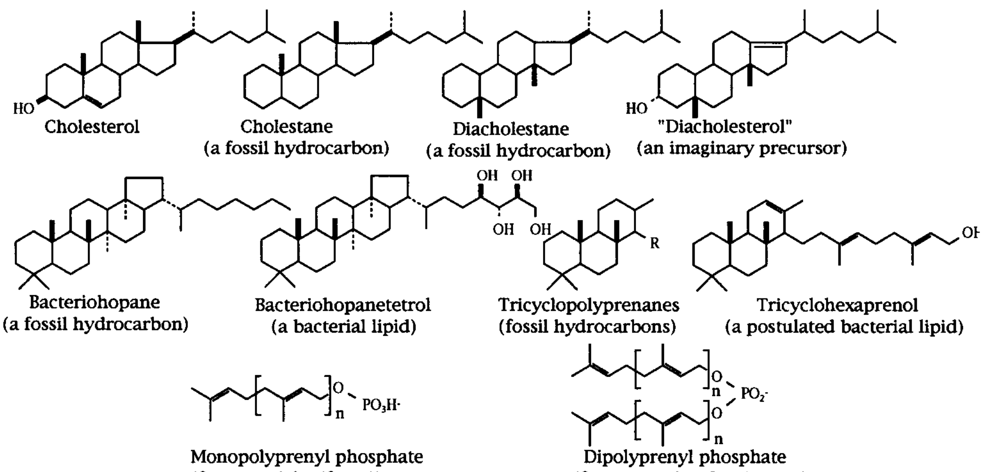
cholesterol does in eucaryotic ones ; this has now been demonstrated, by us and others.

Other molecular fossils form a new catalog of precursor structures, not yet found in Nature but doomed for discovery. Organic geochemistry has thus led to a "predictive microbial biochemistry". All these precursors, like cholesterol, biohopanoids and archeal lipids, could be membrane constituents or membrane reinforcers : they are amphiphilic, with dimensions either about 6 x 6 x 18 Å, with one polar head, or 6 x 6 x 36 Å, with two polar heads. They also happen to be all terpenoids.

Next, we have ordered all these structures into a phylogenetic tree, with branchings representing the recruitment of new enzymatic steps. Cholesterol represents the most evolved structure, with the maximum number of enzymatic reactions, and the requirement of dioxygen.

Retracing backwards the evolution of these membrane constituents, we concluded that the least demanding hypothetical ones could be polyterpenyl phosphates. These have been synthesized, and shown to produce indeed closed vesicles, not very stable but amenable to a detailed physical study. We postulate that these might represent the most primitive membrane constituents ; they could have been formed abiotically from simple precursors.

We are now studying the progressive complexification of these vesicles, by inclusion into their lipidic layer of lipophilic substances, and by virtue of their intrinsic anisotropy : "cytomimetic" chemistry à la Menger.



Reviews :

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