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MODELING OF ABIOTIC SYNTHESIS OF SUGAR ALCOHOLS (GLYCOL, GLYCEROL AND OTHER POLYOLS) AS STRUCTURAL UNITS OF BIOLOGICAL MEMBRANES

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Abstract. The assumption that sea water is the cradle of the origin of primitive living organisms is beyond doubt. No one knows how this happened, but there are many assumptions, although the evidence base for all these assumptions raises many questions. This article is an attempt to elucidate the origin of the protomembrane and its transformation into a bilayer lipid membrane in an inanimate substance. Presumably, protomembranes consisting of fatty acids and other amphiphiles were a simple type of membrane, but with the advent of polyols and, accordingly, complex lipids, a new type of protomembranes appears. Perhaps this new type of protomembrane, consisting of complex lipids, was the beginning of the emergence of the future biological membrane and all life on Earth. Coacervates from the Oparin – Haldane hypothesis were used as a model to explain the formation of protomembranes. The chemical model shows which polyols could spontaneously form in the primary broth, and the mathematical model shows that ethylene glycol (40%), glycerol (33%), butane-1,2,3,4-tetraols (17%) account for 90% of all polyols produced. This indicates the possible predominance of diol lipids in the primary primitive protomembranes. During chemical evolution and with changes in temperature, pH, and environmental conditions, diol lipids were replaced by glycerolipids, which have more suitable physicochemical characteristics for the formation of biological membranes of all living organisms. The article presents polyols as part of complex lipids that are found in modern biological membranes.
Key words: evolution, coacervates, Oparin – Haldane hypothesis, lipids, protomembranes, polyols.

1. Introduction

It is difficult to estimate the time when the first pseudo-living beings appeared from inanimate substances with a protomembrane, but we can say for sure that this time was. The protomembrane is one of the greatest events in the history of coacervates and the evolution of all living organisms [1-6]. Apparently, one of the first steps in the emergence of life was the formation of a membrane, a physical boundary that makes it possible to keep various molecules in concentrated aqueous solutions. It is currently believed that the protomembrane was formed by self-assembly of simple, readily available amphiphiles such as short chain fatty acids, fatty alcohols and/or alkylamines [2-7]. Protomembranes formed from such

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simple lipid molecules (see **Fig. 1**) can be attributed to the primitive class of primary membranes. Apparently, such protomembranes could exist both in primitive living organisms and simply be in an aqueous solution.

The membranes formed by fatty acids and their derivatives can be classified as primary membranes, however, a subsequent or parallel step should be the formation of complex lipids containing low molecular weight polyols. And already complex lipids formed from polyols and fatty acids, or fatty alcohols could form a new type of protomembrane.

It is known that the length, rings, unsaturation, or the presence of heteroatoms in the hydrophobic tails of fatty acids or fatty alcohols significantly affect the physical and chemical properties of membranes [2, 3, 7]. Various aspects of membranes and their lipid molecules, as well as their possible evolution, have been intensively discussed in the scientific literature, and this topic is not discussed in this paper [1, 2, 5].

We can say that there are no reliable data on protomembranes, and only based on our knowledge of the biological membranes of living organisms, we can assume or model processes that may have taken place in the history of our planet [6, 7]. Modern biological membranes are boundary structures of molecular dimensions located on the surface of cells and subcellular particles and consisting mainly of complex lipids [8-10]. The complex lipids of biological membranes are predominantly glycerolipids such as phospholipids, glycolipids, betaine lipids, and other lipids [11, 12].

This article is devoted to low molecular weight polyols and their role in the formation of a protomembrane consisting of a lipid bilayer of complex lipids. In addition, an analysis of polyols found in biomembranes of modern living organisms is presented.

2. Philosophical model

The origin of life on Earth is one of the fundamental tasks of the modern chemical and biological science, has occupied the minds of mankind for more than 100 years, and is consecrated in many famous publications [13-19]. The most prominent among modern scientists use the *Oparin – Haldane hypothesis* about the origin of life on Earth. According to this hypothesis, life came from inanimate matter because of complex biochemical reactions (abiogenic synthesis) [20-24].

2.1. The Oparin – Haldane hypothesis

In 1924, Alexander Oparin suggested that biopolymers (or macromolecular compounds) dissolved in water, under the influence of external factors, can form coacervate drops or coacervates (organic-rich droplets, see **Fig. 2**). These are organic substances gathered, which are conditionally separated from the external environment and begin to support metabolism with it. The process of coacervation – the separation of the solution with the formation of coacervates – is the previous stage of coagulation, i. e., sticking together of small particles. It is because of these processes that amino acids, the basis of living organisms, emerged from the "primary broth" [25-31].

In 1929, regardless of Oparin, John Burdon Sanderson Haldane began to develop similar ideas on the problem of the origin of life. Unlike Oparin, Haldane suggested that instead of coacervates, macromolecular substances capable of reproduction were formed. Haldane believed that the first such substances were not proteins, but nucleic acids [32-37].

2.2. The Miller – Urey experiments

To test the Oparin-Haldane hypothesis about the evolution of prebiotic chemicals and the origin of life on Earth, Stanley Miller under the supervision of Harold Urey set up an experiment that was supposed to answer the main question, is it possible? [38, 39]. The *Miller–Urey experiment* was a simple chemical experiment that simulated conditions on the early prebiotic Earth and tested the chemical origin of life under those conditions. A mixture of methane, ammonia, hydrogen, and water vapor in a closed volume was treated with ultraviolet radiation, simulating the Sun. Scientists examining sealed samples from the original experiments after Miller's death showed that Miller's original experiments produced more than 20 different amino acids that naturally occur in the genetic code. In addition, recent experiments with prebiotics continue to produce racemic mixtures of simple and complex organic compounds under various conditions. An experiment at the time confirmed Oparin-Haldane's hypothesis that supposed conditions on the primitive Earth favored chemical reactions that synthesized more complex organic compounds from simpler inorganic precursors [40-42].

2.3. General conclusions

This is the specificity of this concept: a certain position in the problem of the essence of life can be taken only depending on the solution of the issue of origin and vice versa. We will try to comprehend the problem through history (the logic of discussions) and understand at what level of concrete scientific research is the solution to the problem of the origin of life. We focus on the methodological and ideological aspects of solving the problem in the concept of biochemical evolution. Most of the considerations on which these theories are based are speculative, since it is impossible to reproduce in any visual form the events that occurred when life arose. This applies to both scientific and theological constructions. However, the concept of biochemical evolution, more and more perceived not as a kind of metaphysical theory, but as a set of scientific hypotheses, each of which is verifiable.

It is assumed that in the coacervates themselves, the chemicals included in them entered chemical reactions. On the border between the coacervates and the external environment, lipid molecules were lined up, which led to the formation of a primitive cell membrane providing stability to the coacervates. As a result of the inclusion in the coacervate of a molecule capable of self-reproduction, a primitive cell could arise. Such a supposed sequence of events was supposed to lead to the emergence of a primitive self-reproducing organism, which was "fed" with the organic substances of the primary broth [43-45].

Meteorite samples contain more than 50 cyclic and acyclic monoamine alkanoic and alkanoic acids, alcohols, aldehydes, ketones, sugar-related compounds, and other organic compounds [46, 47]. Among the important acids were found protein amino acids such as alanine, as partic acid, glycine, glutamic acid, leucine, valine, proline, as well as non-protein amino acids [46]. Volatile alkanes such as methane, ethane, propane, isobutane, butane, ethene and normal alkanes with chain length C12-C26 have also been found in carbonaceous chondrites [47]. Numerous studies of meteorites have shown that complex lipids have not been found, although fragments of complex lipids, mainly ether lipids, have been found in marine sediments. This type of lipid is characteristic of Archaea. Complex lipids are the waste product of living organisms [48, 49].

The Oparin-Haldane hypothesis has won many supporters. But it has a significant disadvantage – it cannot explain how a qualitative leap from non-living to living things took place, and how and what functions lipid molecules had, and what they were. One of the fundamental factors in the formation of primitive organisms is the design and formation of the biological envelope (or biological membrane) and its evolution [50-53].

2.4. The role of natural amphiphiles in the formation of the protomembrane

There is no information and evidence of what the protomembrane was, although this information is very important for understanding the origin and evolution of living organisms. However, the accumulated knowledge in science over the past 200 years allows us to simulate processes that may have taken place billions of years ago.

Fatty acids, as one of the main natural amphiphiles, have been found in various geological rocks, marine and freshwater sediments, and meteorites have also been found [1-3, 46, 47]. Fatty acids, their derivatives and other amphiphiles (see **Fig. 1**) are surfactants that, by concentrating at the interface, cause a decrease in surface tension. A common feature of such compounds is that their molecules contain separate atomic groups that interact differently with the dissolving medium and can spontaneously form micelles, or primitive membrane films. Based on this knowledge, it can be suggested that primitive protomembranes (see **Fig. 3**) were composed of fatty acids (A), or that these membranes contained other amphiphiles in addition to fatty acids (B). Coacervates or coacervate drops could acquire such primitive membrane layers (C and D). Thus, natural fatty acids and other amphiphiles were the first components of primitive protomembranes, and this is their principal role. Such a membrane was not very stable and had torn holes, but, nevertheless, it created micelles in which various chemical reactions took place.

2.5. A new type of the protomembrane is a prototype of a biological membrane

To create a new type of protomembrane consisting of complex lipids, low-molecular polyols were needed. The synthesis of these polyols and the formation of a sufficiently large pool of these molecules is described in a chemical model. This pool mainly included ethylene glycol, glycerol, and butane-1,2,3,4-tetraols (see **Fig. 4**), although other polyols with hydroxyl groups from 5 to 8 were in this pool. Ethylene glycol, glycerol, and butane-1,2,3,4-tetraols, and other polyols with fatty acids formed complex lipids where sugars were the polar heads, since there was an abundance of them in the pool, according to the chemical model.

The formation of complex lipids took place by the reaction of various polyols with fatty acids, thus forming neutral lipids. In parallel with this scheme, the synthesis of simple glycolipids took place, that is, sugars were combined with fatty acids, or other amphiphiles. There are many such simple glycolipids in nature. The presence of sugars and neutral lipids at the appropriate temperature, pH, the presence of metal ions, or other activators contributed to the formation of complex glycolipids. Apparently, under certain conditions of the reaction medium, these reactions proceed spontaneously [2-4, 7].

Thus, the first complex lipids were glycolipids. Glycolipids formed both monolayer and/or bilayer membranes, and the contents of coacervates were already inside the lipid layer. Apparently, the transition from a primitive monolayer membrane consisting of fatty acids and amphiphiles to a lipid bilayer consisting of glycolipids is the starting point in the transformation of a new protomembrane into a biological membrane. In a closed space, organic and inorganic simple and complex components surrounded by a bilayer lipid membrane began the formation of complex molecular structures such as RNA or DNA.

The question of acyl or alkyl lipids is especially important since the physicochemical properties of the membrane depend on their structure. It is our understanding that this issue requires a new work and is not discussed. For readers, we give literature that they could read [1-4]. In addition, fatty acids themselves, their derivatives, or alcohols are simple lipids, as you know, and to become complex lipids they must interact with polyols.

Of course, the bilayer lipid membrane of coacervates, consisting of glycolipids, is not a biological membrane, but only creates the prerequisites for the synthesis of proteins or peptides. Any reaction needs energy, and what mechanism was launched for these purposes is not yet entirely clear. **Fig. 5** shows that during evolution, the glycolipids on the inside of the membrane were replaced by phospholipids, and for this it was necessary to have amino alcohols and phosphoric acid. Whether this process already took place in living protocells or whether it was still a process of chemical evolution of a non-living substance is not yet known.

Coacervates were able to absorb substances from the outside as open systems. When different catalysts were included in them, different reactions occurred. Due to this, coacervates could increase in volume and weight, and then split into daughter formations. Thus, coacervates could grow, multiply, and carry out metabolism. It remains an open question how such complex "machines" as primordial DNA and the complex of protein-enzymes necessary for its functioning could spontaneously arise.

The additions that we made to the Oparin-Haldane hypothesis and the Miller-Urey experiments allow us to take a fresh look at the topic of coacervates and protomembranes. Below we present the chemical and mathematical models that explain the conclusions we made in the philosophical model.

3. Chemical Model

The chemical model that we present is a well-accepted scheme for the formation of low-molecular polyols with the number of carbon atoms from two to eight. In addition, these polyols can cyclize to form simple sugars. Monosaccharides or polyhydroxyaldehydes with five, six, seven or eight carbon atoms, which are classified as pentoses, hexoses, heptoses or octoses, form low molecular weight polyols according to the proposed chemical model (**Fig. 6**).

3.1. Formation of ethylene glycol, glycerol, and other polyols

As early as 1861, Russian chemist Alexander Butlerov [54-56] showed that formaldehyde in aqueous solutions in the presence of calcium and barium hydroxides produced a complex mixture of monosaccharides. Subsequently, almost all common hexoses, pentoses, tetroses and trioses were identified [57, 58].

Subsequently, this reaction was called its own name as *Butlerov's reaction* [59]. The synthesis begins with the formation of glycolaldehyde, and it is this reaction that limits the overall speed of the process. The mechanism of ethylene glycol synthesis is still not well understood, although there are many of its variants based on the free radical interaction of methanol and formaldehyde [60-63]. However, it is known that, as soon as enough glycolaldehyde has accumulated, an autocatalytic process begins, which in a short time involves all the available formaldehyde in the reaction; in this case glycerin aldehyde, tetrose, pentose and hexose are formed. The functioning mechanism in this case is the alkali-catalyzed aldol condensation process. The synthesis of glyceraldehyde from formaldehyde was proposed in 1959 by Breslow, and other schemes for its synthesis also exist [64-69].

Thermodynamic conditions indicate that the conversion of formaldehyde to glyceraldehyde can take place even at low concentrations [70]. Metal ions catalyze this reaction by forming complexes [66, 71]. Under abiotic conditions, glyceraldehyde plays the central role of an intermediate in the chemical processes of primary life in the proposed of amphiphilic components and their role in the evolution of membrane structures in the primeval Earth, this has already been done [20, 85]. This model considers only the formation of low molecular weight polyols – the structural blocks of complex lipids. This article does not describe how the molecules of complex lipids were formed but provides data on their presence in the biological membranes of living organisms. Some options for the synthesis of simple lipids and speculation on that topic have previously been described by us and some other authors [1, 2, 7, 21-24].

3.2. Graphic implementation of polyol formation

Monosaccharides containing an aldehyde group in an open form, starting from tetrose, are prone to cyclization, which prevents the carbonyl group from further attack by formaldehyde or glycolaldehyde anions (**Table 1**), and monosaccharides that are in a cyclic form, furanose or pyranose, leave the further reaction and thus way interrupt the formation of polyols with many hydroxyl groups. The reduction of the aldehyde group of aldose leads to the formation of the corresponding polyols (ethylene glycol, glycerol, and others). The reduction process can occur under the action of hydrogen in the presence of nickel, copper, ammonia, or hydrogen sulfide, as well as some other reducing agents [72, 86-88].

4. The mathematical model of polyol formation

triose Weber model [72–74]. The formation of diacyl lipids from low molecular weight polyols was discussed in detail in the work [2, 7, 18, 50-52, 75, 76], and the formation of alkoxylipids (ether lipids) was considered by us earlier [1].

That is why we will not discuss the formation

The mechanism of formation of polyols described in the chemical model does not show in what proportion low molecular weight molecules are synthesized during these chemical reactions. For these purposes, we have proposed a mathematical model that gives us a possible idea of the proportions of low molecular weight polyols in the synthesis of complex lipids.

Thus, if we adopt a consistent scheme of random formation of various polyols, then on its basis we can propose the following mathematical model [83-87].

Low molecular weight alcohols with the number of hydroxyl groups from two to eight are the backbone of complex lipids. Let us assume that the formation of these polyols can be represented as a sequential random process of "*increasing*" the number of hydroxyl groups by selecting them from some common pool, when some random time T is spent "*search*" for the next hydroxyl group.

Then a single observation over the system of an infinite number of independent, identically distributed random variables T_0, T_1, T_2 ... (T, is the random time of the "search" of the hydroxyl group) will be denoted by t_0, t_1, t_2 ...

The value of t_n is called the turning point of the maximum type if the relation

$$t_{n-1} < t_n = t_{n+1} = \ldots = t_{n+k-1} = t_{n+k} > t_{n+k+1} \quad (1)$$

Before conducting a thought experiment, the number of hydroxyl groups between two adjacent turning points of the maximum type is a random variable Q with the following distribution law [83, 84]:

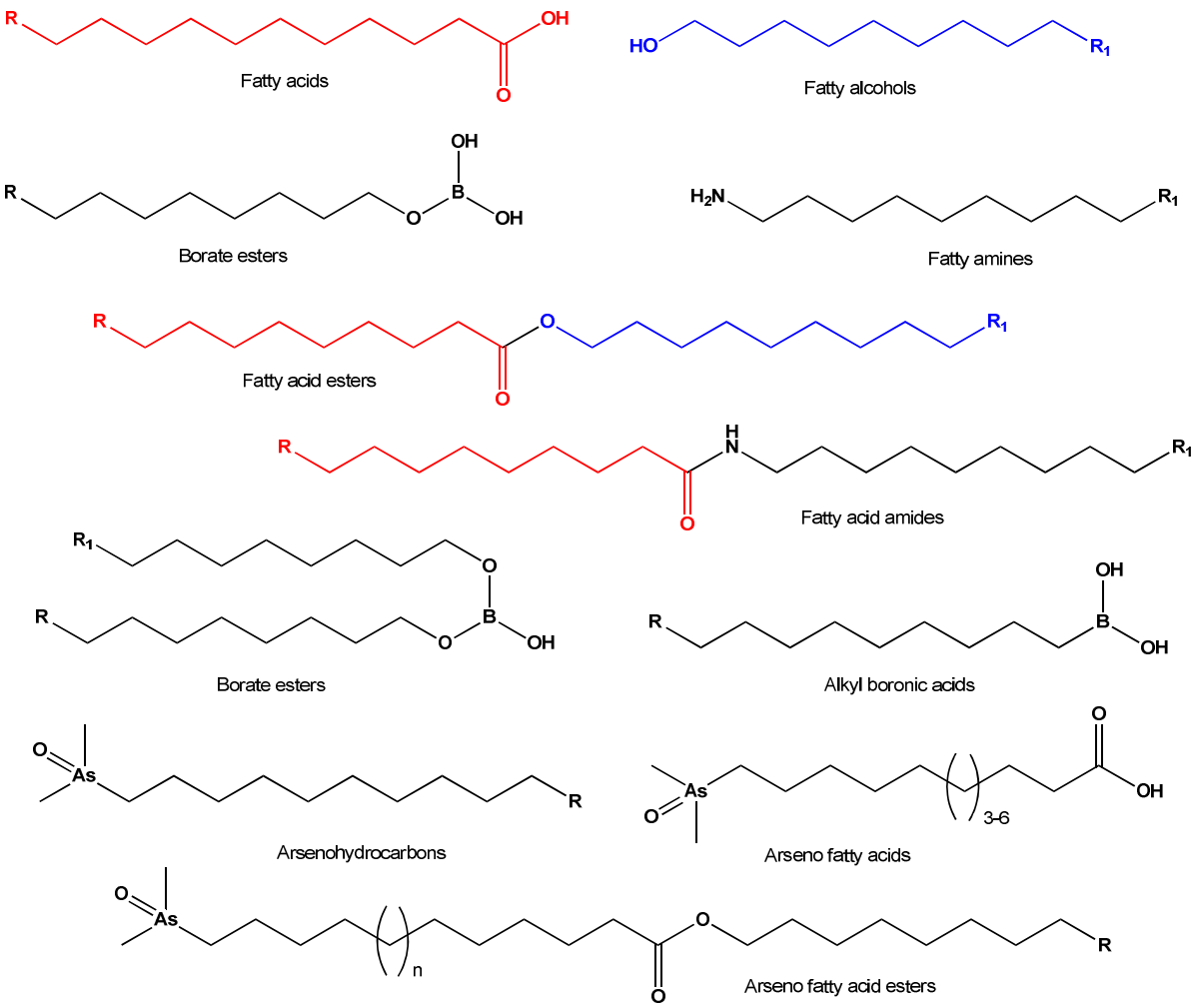

Figure 1. Examples of some natural amphiphilic compounds forming stable membranes in common temperature ranges and free from chemically bonded polyols.

Fatty acids, fatty acid esters, fatty acid amides, borate esters, alkyl boronic acids or arsenolipids are the most primitive organic compounds capable of forming membranes spontaneously. All the submitted samples were discovered and isolated from various living organisms and their physical and chemical parameters were studied, as well as liposomes were examined. Fatty acids are hydrophobic or amphiphilic (with hydrophilic and hydrophobic parts) macrobiomolecules that are used in living organisms as structural components of the membrane.

Рис. 1. Примеры некоторых природных амфифильных соединений, образующих стабильные мембраны в обычных диапазонах температур и не содержащих химически связанных полиолов.

Жирные кислоты, сложные эфиры жирных кислот, амиды жирных кислот, сложные эфиры борной кислоты, алкилборные кислоты или арсенолипиды являются наиболее примитивными органическими соединениями, способными спонтанно образовывать мембраны. Все представленные образцы были обнаружены и выделены из различных живых организмов и изучены их физико-химические параметры, а также исследованы липосомы. Жирные кислоты представляют собой гидрофобные или амфифильные (с гидрофильной и гидрофобной частями) макробиомолекулы, которые используются в живых организмах в качестве структурных компонентов мембран.

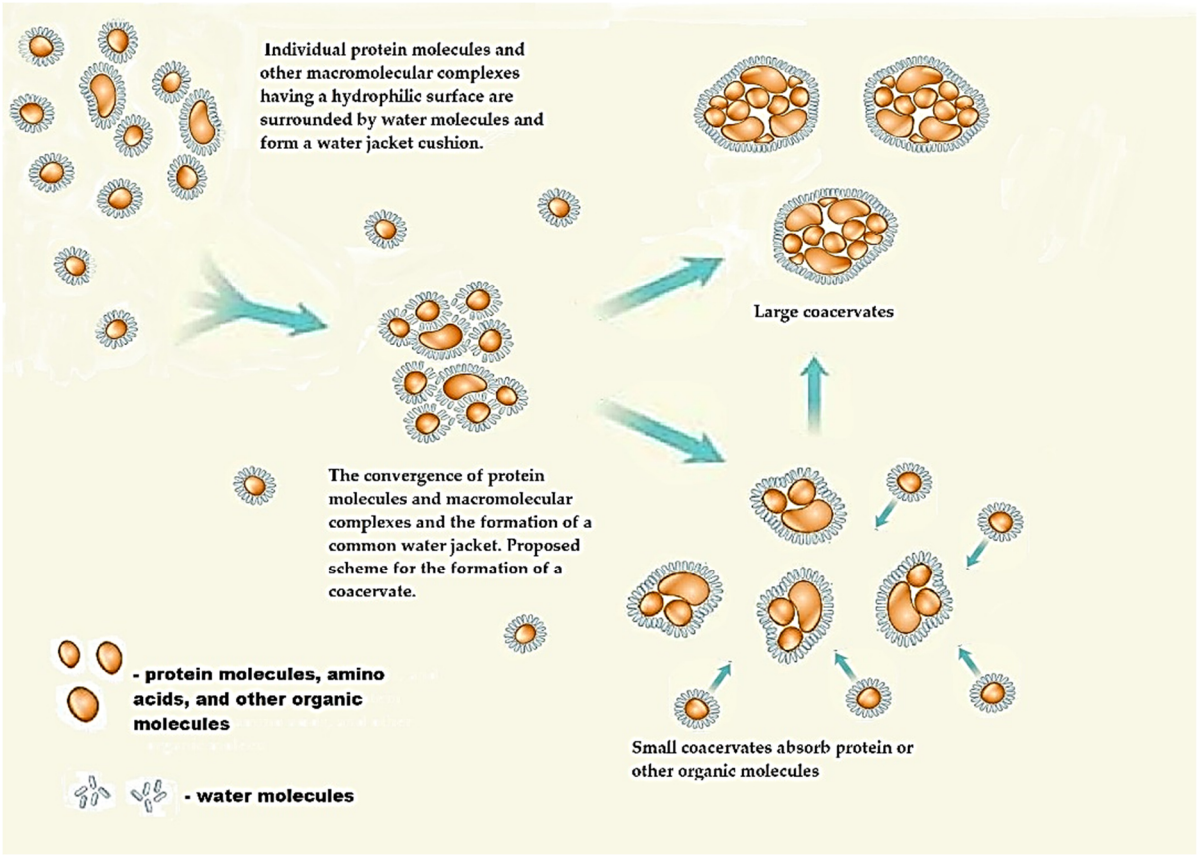

Figure 2. Scheme showing the formation of small and large coacervates in the aquatic environment.

It is known that the term "coacervate" was coined in 1929 by Dutch chemists Hendrik G. Bungenberg de Jong and Hugo R. Kruyt while studying lyophilic colloidal dispersions. Coacervate (translated from Latin means "*collected in a heap*") or "*primary broth*" - a multimolecular complex, drops or layers with a higher concentration of colloid than in the rest of the solution of the same chemical composition.

Рис. 2. Схема образования мелких и крупных коацерватов в водной среде.

Известно, что термин «коацерват» был введен в 1929 г. голландскими химиками Х.Г. Бунгенбергом де Йонгом и Х.Р. Крейтом при изучении лиофильных коллоидных дисперсий. Коацерват (в переводе с латыни означает «*собранный в кучу*») или «*первичный бульон*» — полимолекулярный комплекс, капли или слои с более высокой концентрацией коллоида, чем в остальном растворе того же химического состава.

$$P(q) = \begin{cases} \sum_{i=1}^{(q-1)/2} \dfrac{6i}{(2i+1)!(q-2i)!(q-2i+2)}, & q-odd, \\ \sum_{i=1}^{q/2} \dfrac{6i}{(2i+1)!(q-2i)!(q-2i+2)} - \dfrac{3(q+2)}{(q+3)!}, & q-even. \end{cases} \quad (1)$$

See *supplement* for the complete mathematical derivation of the formula for calculating polyols.

Interesting features of this law are its independence from the probability density of the initial random variable T_1 (in other words, its considerable generality) and the exact equality $M(Q) = 3$, where $M(Q)$ is the mathematical expectation of the number of hydroxyl groups of one polyol. In this scheme, $M(Q)$ is associated with the average "*distance*" between the turning points such as the maximum of the initial random value T - time for the "search" of the hydroxyl group.

According to this scheme, the theoretical distribution of the number of hydroxyl groups in the polyol has the form (see **Table 1**).

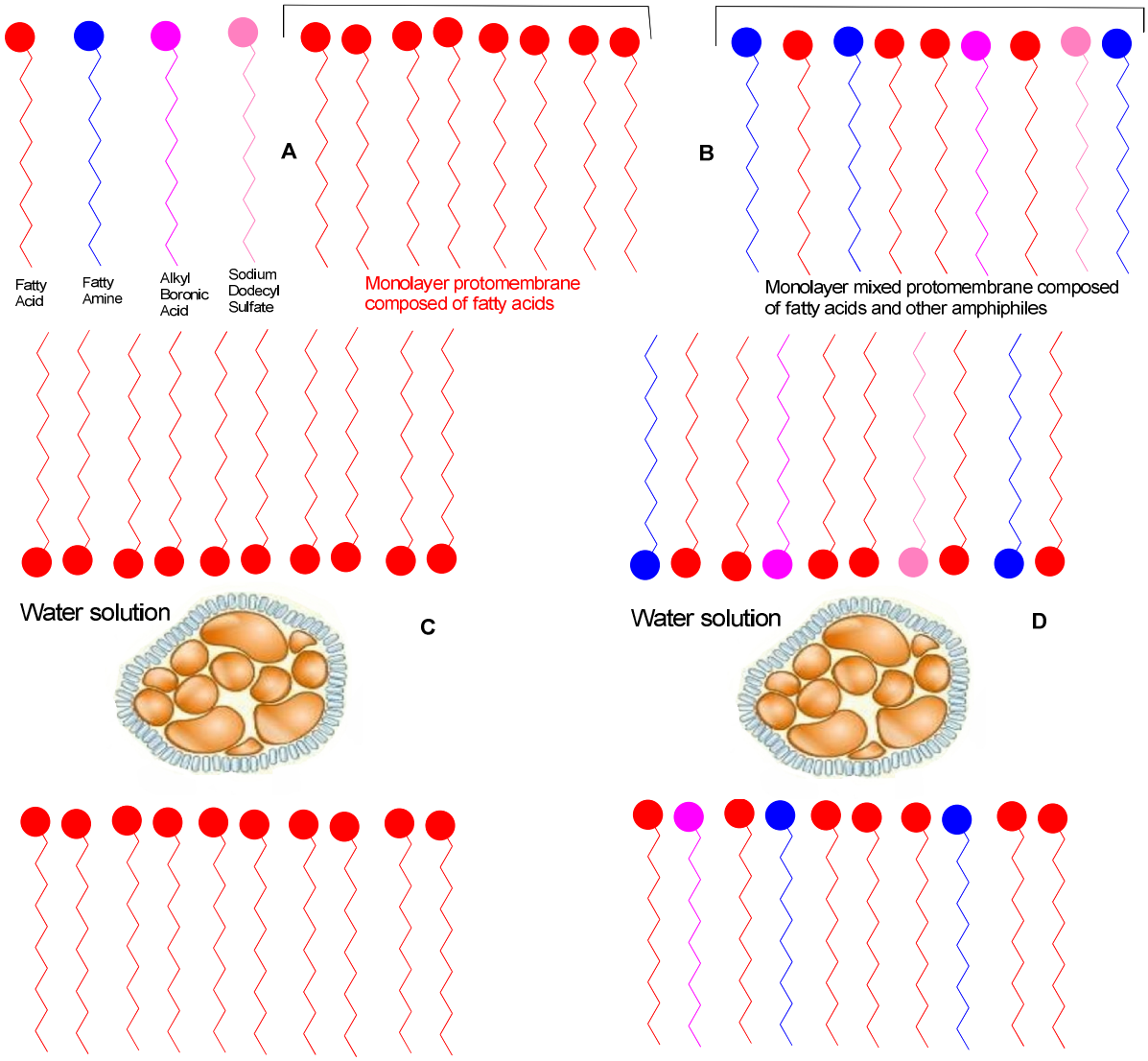

Figure 3. Primitive protomembranes could consist of fatty acids (A) or mixed with other amphiphiles (B).
Coacervates containing proteins, amino acids, and many other organic compounds were separated from the aqueous solution by a primitive fatty acid membrane (C) and included other amphiphiles (D).

Рис. 3. Примитивные протомембраны могли состоять из жирных кислот (A) или смешанных с другими амфифилами (B).
Коацерваты, содержащие белки, аминокислоты и многие другие органические соединения, были отделены от водного раствора примитивной жирнокислотной мембраной (C) и включали другие амфифилы (D).

Table 1. The theoretical distribution of the number of hydroxyl groups in the polyols

Таблица 1. Теоретическое распределение числа гидроксильных групп в полиолах

q	**2**	**3**	**4**	**5**	**6**	**7**	**8**
P(q)	0.400	0.333	0.171	0.067	0.021	0.006	0.001
%	40.0	33.3	17.1	6.7	2.1	0.6	0.1

Abbreviations: q, the number of hydroxyl groups in the polyol; %, the number of hydroxyl groups in the polyol (alcohol), expressed as a percentage. Starting with a polyol with four hydroxyl groups, their quantitative content decreases sharply in percentage, and this is due to the formation of boron complexes.

Thus, under the assumptions made, the abiotic synthesis of polyols should have been carried out according to the above scheme (**Fig. 2**), which explains the predominance of polyols with a lower number of hydroxyl groups (the probability of synthesizing polyols with a few hydroxyl groups of 2, 3 and 4 is more than 90 percent, see **Table 1**).

The mathematical model shows that polyhydric alcohols with the number of hydroxyl groups 2 (ethylene glycol), 3 (glycerol), 4 (1,2,3,4-tetrahydroxybutane) prevailed in protomembranes. And the formation of polyols with the number of hydroxyl groups of 5, 6, 7, 8 is possible, but less likely. Such a low content of polyols with many hydroxyl groups can be explained by the fact that aldoses, the precursors of polyols, are cyclized, thereby interrupting a further increase in the number of hydroxyl groups [84].

According to chemical and mathematical models, polyols with 2, 3 and 4 hydroxyl groups are dominant in both protomembranes and biological membranes. Why such a distribution of polyols appeared, apparently, can be explained by the following phenomenon. Thus, because of reactions (see **Fig. 6**), the resulting sugars and polyols with more than 4 hydroxyl groups easily form boron sugar complexes (I-XIV) and these complexes are removed from the reaction pool. The formation of boron sugar complexes with ethylene glycol, glycerol, and 1,2,3,4-tetrahydroxybutane is also possible, but to a much lesser extent. **Fig. 7** shows some boron sugar complexes with sugars and polyols and these compounds have been found in living organisms [8,88-93].

5. The distribution of low molecular weight polyols in nature

Currently, almost all representatives of low molecular weight polyols are found in biological membranes both in free form and in the form of various lipids that the basis of biological membranes. According to the mathematical model, the primary proto membranes could contain the entire set of polyols in the proportion indicated in **Table 1**.

Complex lipids based on ethylene glycol and glycerol were dominant (more than 73%). In the process of evolution and specialization of proto membranes, glycerolipids occupied a dominant position and they formed the basis of primary biological membranes. Can we simulate this long-term process in the laboratory – we can say no. However, a conceptual understanding of this process can be assumed. Below we present experimental data that confirm that the polyols given in this article are found in nature, however, their proportional distribution in living organisms should differ from their primary proto membranes.

Low molecular weight polyols and especially such as ethylene glycol, glycerol, erythritol/threitol and others have been found in nature however in very small quantities. First, this is explained by the physicochemical characteristics of ethylene glycol and glycerol. Comparative the physicochemical characteristics of ethylene glycol and glycerol and polyols containing four hydroxyl groups are presented in **Table 2.**

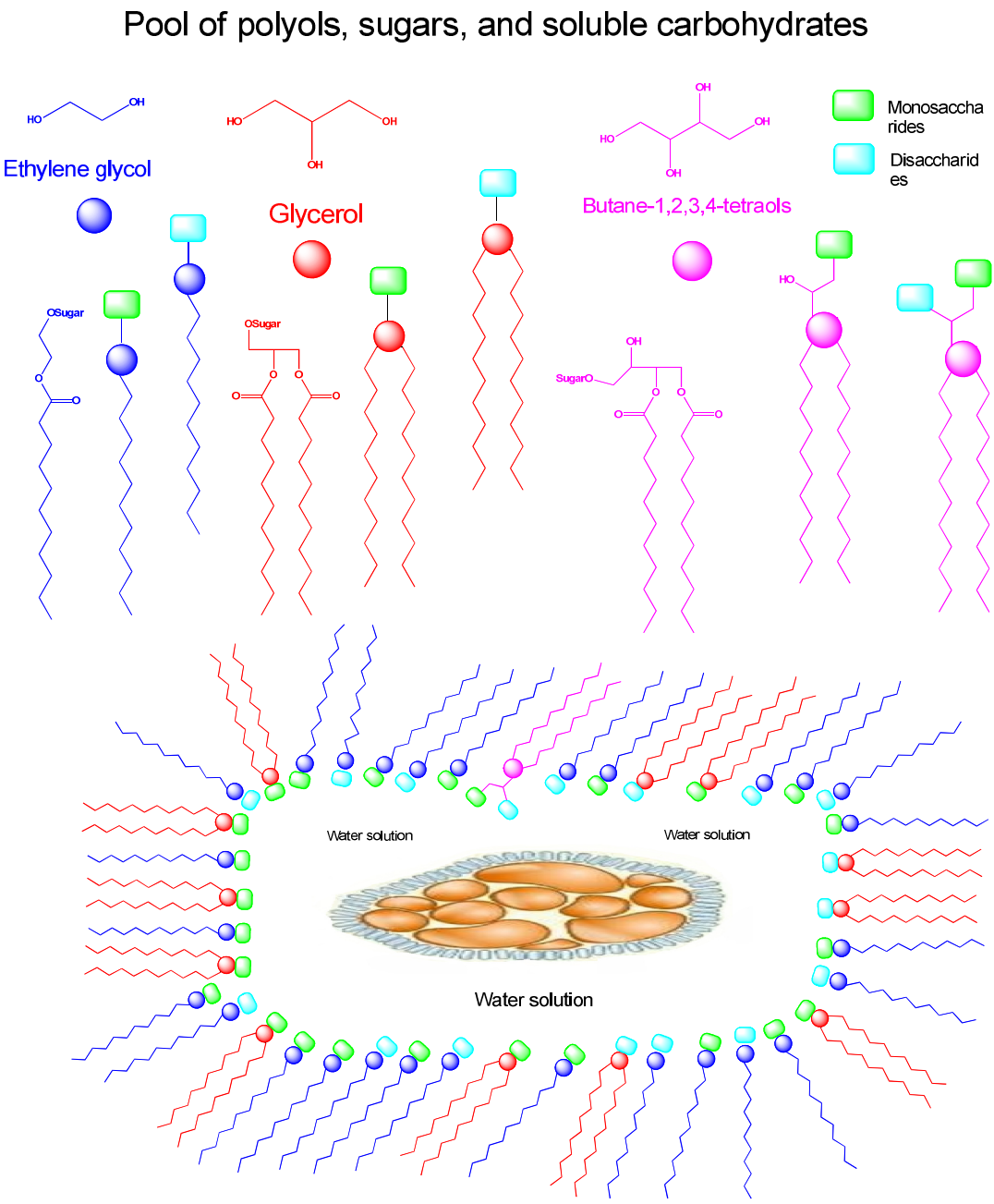

Figure 4. According to the chemical model, a pool of low molecular weight polyols with 2 to 8 hydroxyl groups was formed, as well as sugars, and soluble carbohydrates.

Fatty acids, polyols, and sugars formed complex lipids - glycolipids. These glycolipids were wrapped in a film of coacervates or coacervate drops, that is, *de facto*, a bilayer lipid membrane appeared in coacervates.

Рис. 4. Согласно химической модели, образовался пул низкомолекулярных полиолов с количеством гидроксильных групп от 2 до 8, а также сахаров и растворимых углеводов.

Жирные кислоты, полиолы и сахара образуют сложные липиды – гликолипиды. Эти гликолипиды были завернуты в пленку коацерватов или коацерватных капель, то есть де-факто в коацерватах появилась двухслойная липидная мембрана.

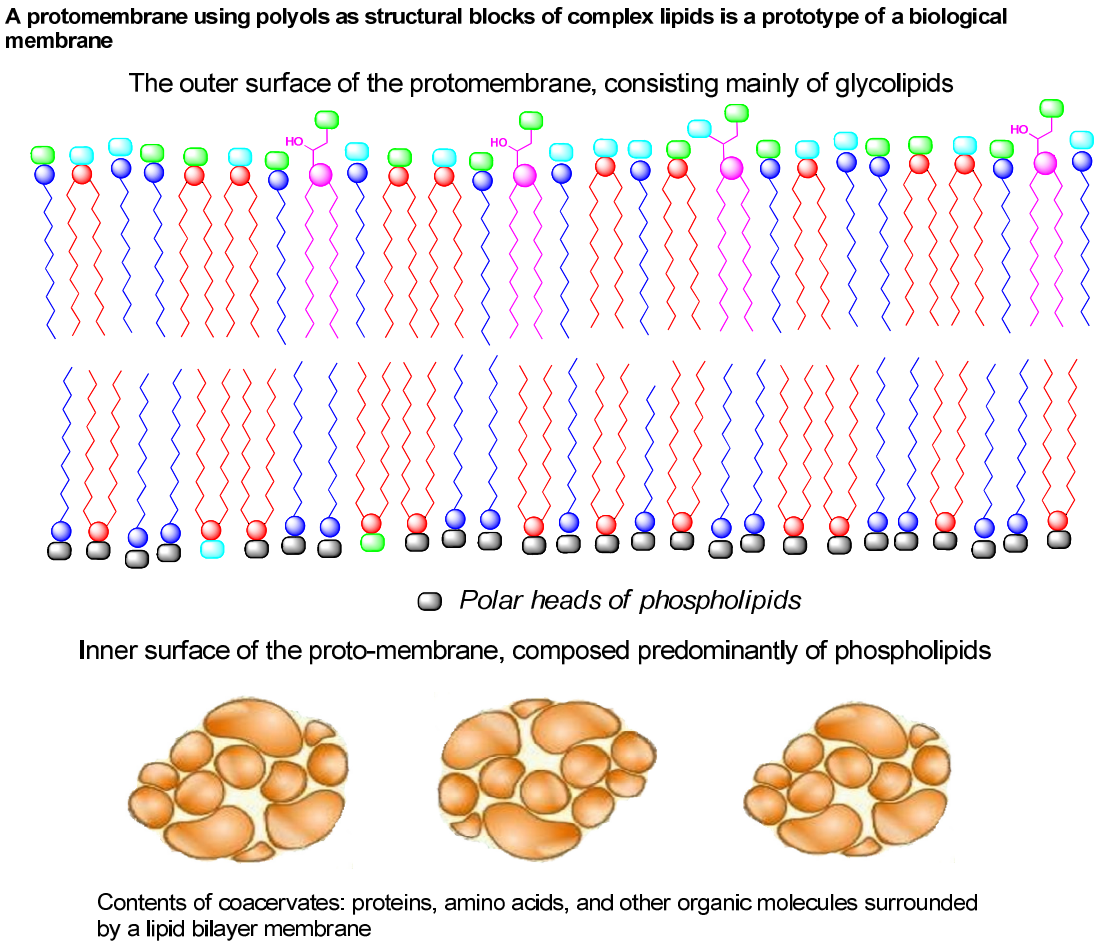

Figure 5. Bilayer lipid membrane composed of glycolipids on the outside and phospholipids and glycolipids on the inside.

This membrane, apparently, is not yet a biological membrane, but is a coacervate membrane.

Рис. 5. Двухслойная липидная мембрана, состоящая из гликолипидов снаружи, и фосфолипидов, и гликолипидов внутри.

Эта мембрана, по-видимому, еще не является биологической мембраной, а представляет собой коацерватную мембрану.

Table 2. Comparative physical properties of ethane-1,2-diol, propane-1,2,3-triol, and butane-1,2,3,4-tetraols at 20°C*

Таблица 2. Сравнительные физические свойства этан-1,2-диола, пропан-1,2,3-триола и бутан-1,2,3,4-тетраолов при 20°C*.

Properties	Ethylene glycol	Glycerol	Erythritol	Threitol
Chemical formula	$C_2H_4(OH)_2$	$C_3H_5(OH)_3$	$C_4H_6(OH)_4$	$C_4H_6(OH)_4$
Molecular mass	62.07	92.09	122.12	122.12
Melting point, °C	−12.9	18.2	121.0	88 to 90
Boiling point, °C	197.3	290.0	329 to 331	330.0
Critical temp., °C	372.0	577.0	819.9	820
Freezing point, °C	−13.0	17.8	119.7	119.9
Density, g/cm^3	1.11	1.26	1.45	1.47
Surface tension, mN/m	48.5	64.0	80.9	80.9
Viscosity, x 10^{-3} Pa s	18.37	1.412	0.0612	0.069

*Comparative physical properties are taken from open sources, and anyone can find this information if they are interested in the properties of these polyols.

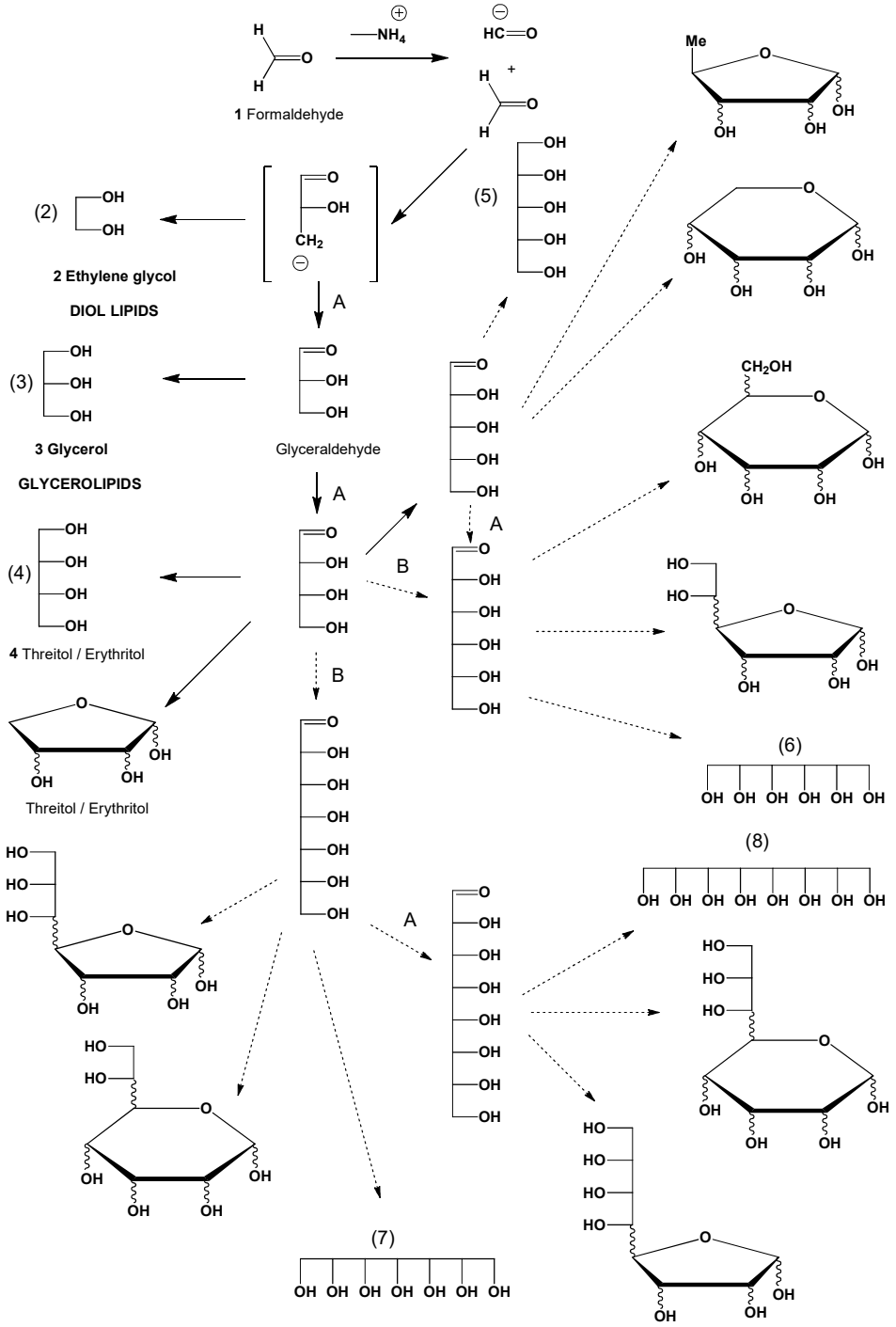

Figure 6. Chemical model of the synthesis and formation of polyols during evolution.
The proposed path of abiotic synthesis of polyols with the number of hydroxyl groups (number in brackets) from 2 to 8 from formaldehyde. A – the way of increasing the subsequent polyol by the -CH_2OH group, B – the way of increasing the subsequent polyol by the -$CH_2OHCH_2OHCH_2OH$ group.

Рис. 6. Химическая модель синтеза и образования полиолов в процессе эволюции.
Предложен путь абиотического синтеза полиолов с числом гидроксильных групп (число в скобках) от 2 до 8 из формальдегида. А – способ наращивания последующего полиола по группе -CH_2OH, Б – способ наращивания последующего полиола по группе -$CH_2OHCH_2OHCH_2OH$.

6. Ethylene glycol (ethane-1,2-diol) and diol lipids

In recent years, it has been discovered that in several lipids, the role of the "central" structural fragment (in addition to glycerol) can be played by diatomic alcohols (diols) of various structures. Therefore, such lipids are called diol lipids (see **Fig. 8-10**).

An interesting question is about the so-called ether lipids, which are widely distributed in nature. We do not consider this issue in this article, since this was discussed in the literature, as well as the formation and biotransformation of these lipids, we described in detail earlier [1].

Diol lipids are linear alkanes of different lengths containing two hydroxyl groups at the α- and β-positions [94-104]. An interesting question is about diol lipids, and are these lipids "prebiotics"? No one can answer this question unambiguously. However, it is probably to assume that these most "simple" complex lipids are the same as 3 billion years ago. From a chemical point of view, the hydrophobic "tails" were apparently shorter (C6-C10) than those found in nature (up to C30 and more).

In the 40s of the XX century, Lindberg first isolated 1,2-propanediol phosphate from sea urchin eggs and from the ox brain [105]. Five or ten years later, this trend in lipid chemistry has made significant progress, and propanediols, butanediols and/or their phosphates have been found in various mammalian organs such as rat livers, cat kidneys, cattle lenses, and rats, and in some cancer tissues [106-110]. Propane-l,2-diol, propane-l,3-diol, Propane-l,2-diol, propane-l,3-diol, butane-l,2-diol, butane-l,3-diol, butane-2,3-diol, butane-l,4-diol, pcntane-l,5-diol, and hexane-l,6-diol have been found not only in mammals, but also in yeasts and fungi such as *Lipomyces* sp., *Streptomyces toyocaensis, Candida tropicalis, C. polymorpha, Pichia wid-terhami, P. pseudopolymorpha* and *Debaromyces hansenii* [94,95].

However, for us the most interesting are diol lipids, the backbone of which is ethylene glycol (or ethane-1,2-diol). The most abundant diol lipids are found in bacteria such as *Corynebacteria diphteria, Mycobacterium avium, Mycobacterium bovis* and *Brucella mellitensis* [111-113].

The neutral diol lipids are 1-O-acyl-ethylene glycols, 1-O-alkyl ethylene glycols, 1-O-alkenyl ethylene glycols, which were isolated from natural sources. Thus, 1-O-acyl-ethylene glycols (**24-28**, structures are shown in the **Fig. 3**) were found in extracts of seeds of corn and sunflower and some plant species [94, 95], and neutral lipids (**24**, **25**, and **28**) were obtained from a Gram-negative coccobacillus bacterium *Brucella melitensis* and a Gram-negative, aerobic, pathogenic bacterium *Bordetella pertussis* [114].

Monochamol (2-undecyloxy-1-ethanol) (**33**) and its analogs 1-O-alkyl ethylene glycols (**29-32**) are pheromones and are synthesized by males of several *Monochamus* species (Cerambycidae) [115-118].

1-O-Acyl ethylene glycols are rare neutral lipids, and yet they have been found and isolated from various natural sources. Thus, (**24-28**, **40-44**) were isolated from a Gram-negative coccobacillus bacterium lipid extract from the Brucellaceae family (*Brucella melitensis* and *Bordetella pertussis*) [114]. In addition, 1-O-acyl ethylene glycols (**24-27, 33-35, 36-39, 45, 46, 48-51**, structures are shown in the **Fig. 9** and **10**) have been found in neutral fractions of seed, plant, and marine invertebrate extracts [94, 95, 119]. In addition, long chain mono- and dialkyl ethers of ethane diol and propanediols were isolated from the jaw oil of the porpoise *Phocoena phocoena* extracts [120, 121].

Diol polar phospholipids (**52-60**, structures are shown in the **Fig. 11**) are found in various organs and tissues of many mammals, and are also found in bacteria, fungi, and plants. A wide variety of these diol lipids have been isolated from extracts of algae and various species of marine invertebrates. These data are summarized and published in several review articles [94, 95, 122].

Tissues of the starfish *Distolasterias nipon* contain large amounts of lipids derived from ethanediol ethers. The neutral lipid fraction yielded, by combined column and thin-layer chromatography, an individual compound of the type 1-alk-1′-enyl-2-acyl ethanediol and a group of saturated 1-alkyl-2-acyl derivatives of ethanediol. Chemical methods showed that the neutral plasmalogen to be the octadeca-1′,9′-dienyl ether of stearoyl ethanediol, while the main components of the saturated fraction were the hexadecyl and octadecyl ethers of stearoyl ethanediol [94, 95]. The high level of ether lipids containing ethanediol (about 35% of the triglycerides) in starfish tissues shows that some organisms are producing diol derivatives as major components of lipid biosynthesis [123]. Unusual glycolipids (**61-65**, structures are shown in the **Fig. 12**) containing ethylene glycol have been detected in ripening corn seeds and other seeds [94, 95, 124, 125].

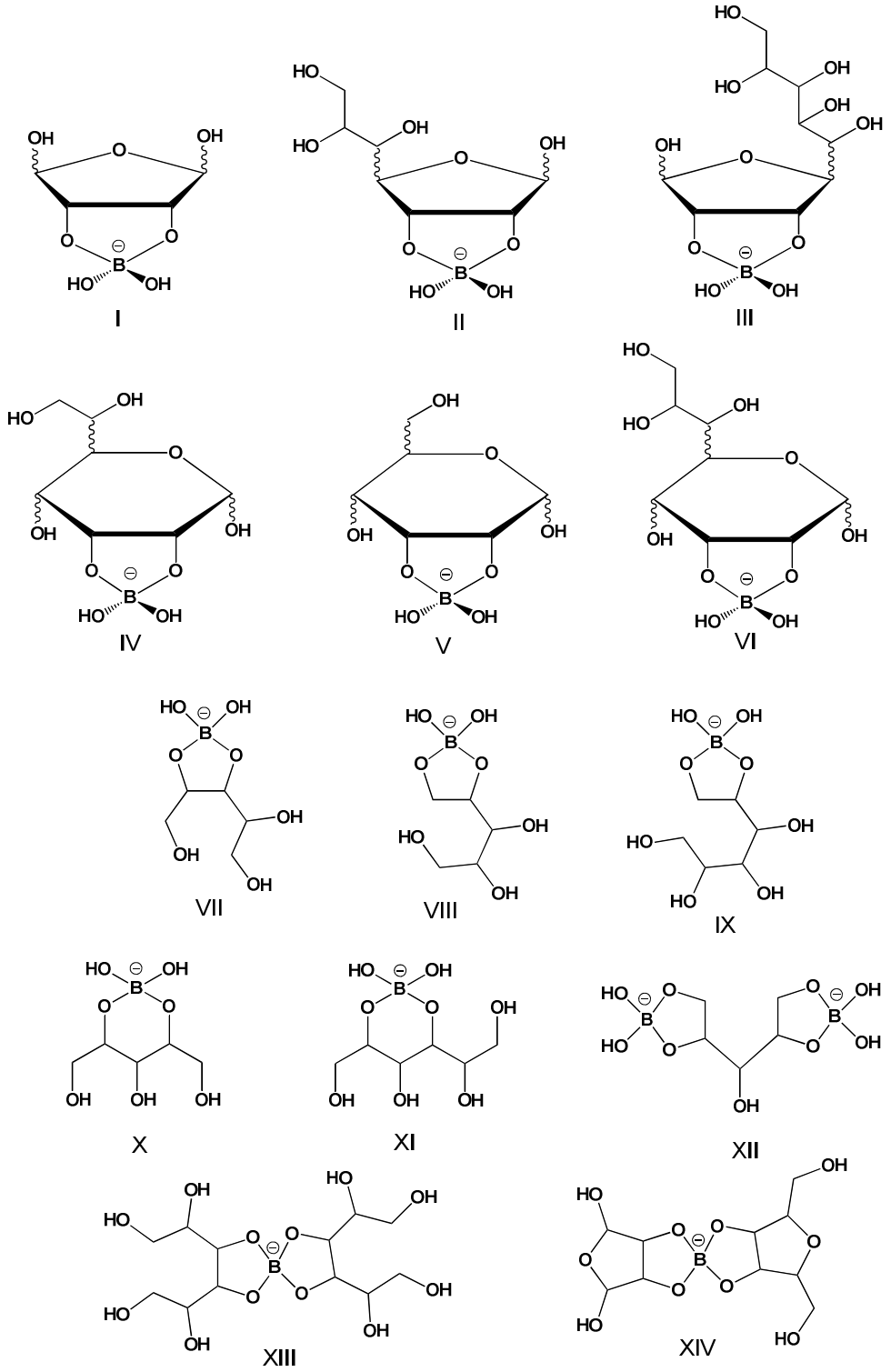

Figure 7. Boron complexes with sugars and polyols with four or more hydroxyl groups, which are easily formed under certain conditions of reaction mixtures.
The boron sugar complexes (**I-XIV**) shown in the figure have been isolated from various natural sources.

Рис. 7. Комплексы бора с сахарами и полиолами с четырьмя и более гидроксильными группами, которые легко образуются при определенных условиях реакционных смесей.
Комплексы бора и сахара (**I–XIV**), показанные на рисунке, были выделены из различных природных источников.

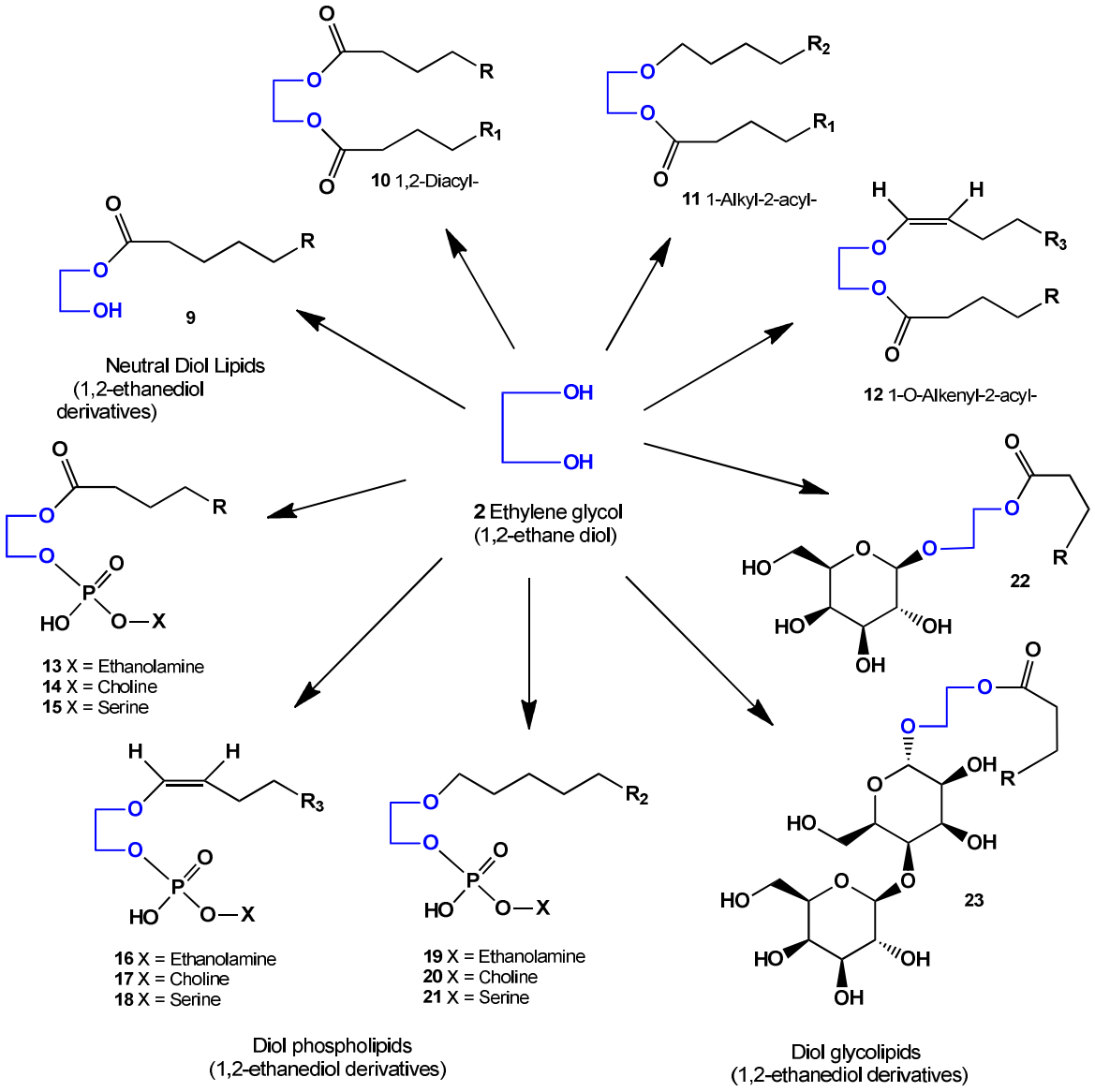

Figure 8. Principal diol lipids, including neutral (9-12), phospholipids (13-21) and glycolipids (22,23) derived from natural sources.

Рис. 8. Основные диольные липиды, включая нейтральные (9–12), фосфолипиды (13–21) и гликолипиды (22, 23), полученные из природных источников.

Unusual polyoxy-ethylene glycol containing glycolipids were isolated from extracts of mycobacteria *Corynebacterium matruchotii* and *Mycobacterium smegmatis* that were cultured on media with the addition of Tween 80. The series 2A (**66**, structures are shown in the **Fig. 13**) and series 2B (**67**) glycolipids contained the polyoxyethylenic acids, trehalose, and corynomycolic acid and were the main compounds in the glycolipid fraction. In addition, glycolipids of series 3A (**68**) and series 3B (**69**) were isolated, which did not contain corynomycolic acid and were minor compounds [126].

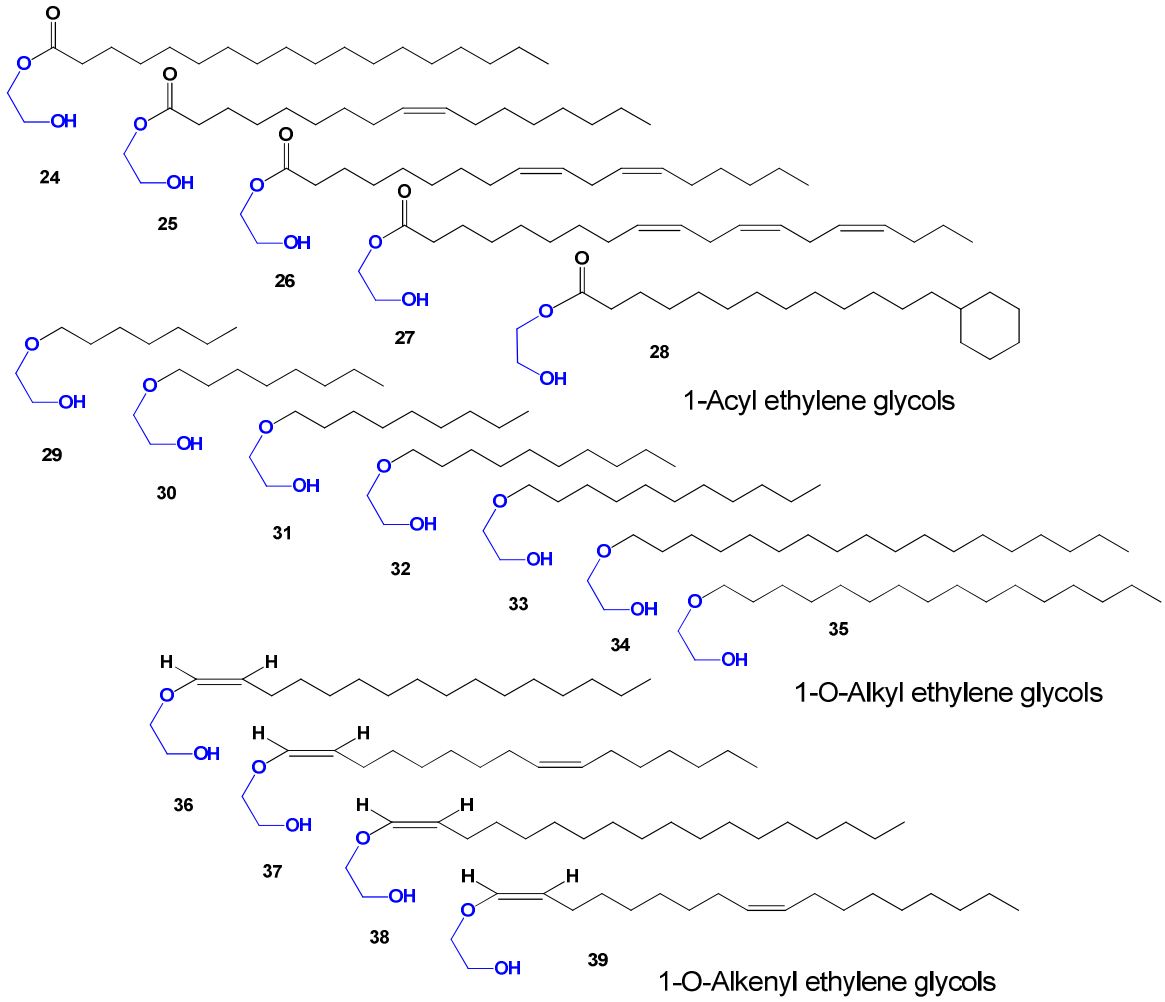

Figure 9. Neutral mono diol lipids derived from natural sources.

Рис. 9. Нейтральные монодиольные липиды, полученные из природных источников.

7. Glycerol (propane-1,2,3-triol) and glycerolipids

Glycerol and complex lipids having it as a "core" are the dominant class of lipids in the organic world. Conceptually, the chemical structures of glycerolipids of biological membranes of living organisms and glycerolipids of protomembranes of coacervates are the same. Differences can only be in the length of the alkyl tails or their unsaturation. Undoubtedly, the hydrophobic "tails" of complex lipids can be so different, and they all have different physical and chemical properties, but they have only one thing in common, that they are glycerides. According to the mathematical model, the content of complex lipids based on glycerol was more than 33 percent of the total of all polyols.

Glycerol (propane-1,2,3-triol) is a viscous, odorless, colorless liquid with a sweet taste. The name glycerol is derived from the Greek word for "*sweet*", *glykys*, and the terms glycerin, glycerine, and glycerol tend to be used interchangeably in scientific literature. In the modern era, it was identified in 1779 by Swedish chemist C.W. Scheele, who discovered a transparent, syrupy liquid when heating olive oil with litharge [127,128].

Glycerol is currently produced by the yeast *Candida glycerinogenes, Debaryomyces hansenii, Dekkera bruxellensis* and *Saccharomyces cerevisiae* [129-134], the marine alga, *Dunaliella tertiolecta*, as well as the grape molds *Aspergillus niger, Penicillium italicum, Rhizopus nigricans*, and *Botrytis cinereal* [135-138].

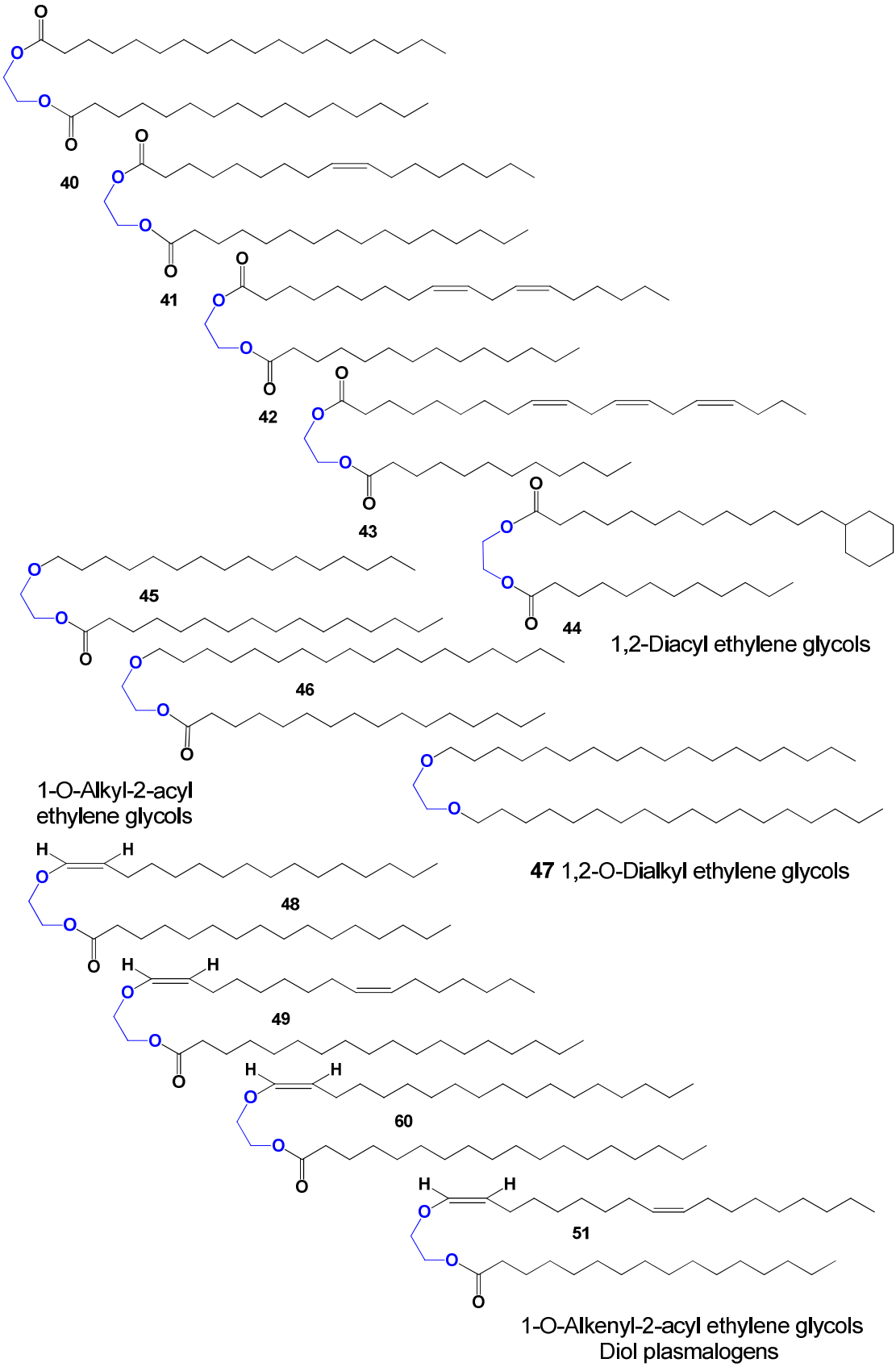

Figure 10. Neutral diol lipids derived from different natural sources.

Рис. 10. Нейтральные диольные липиды, полученные из различных природных источников.

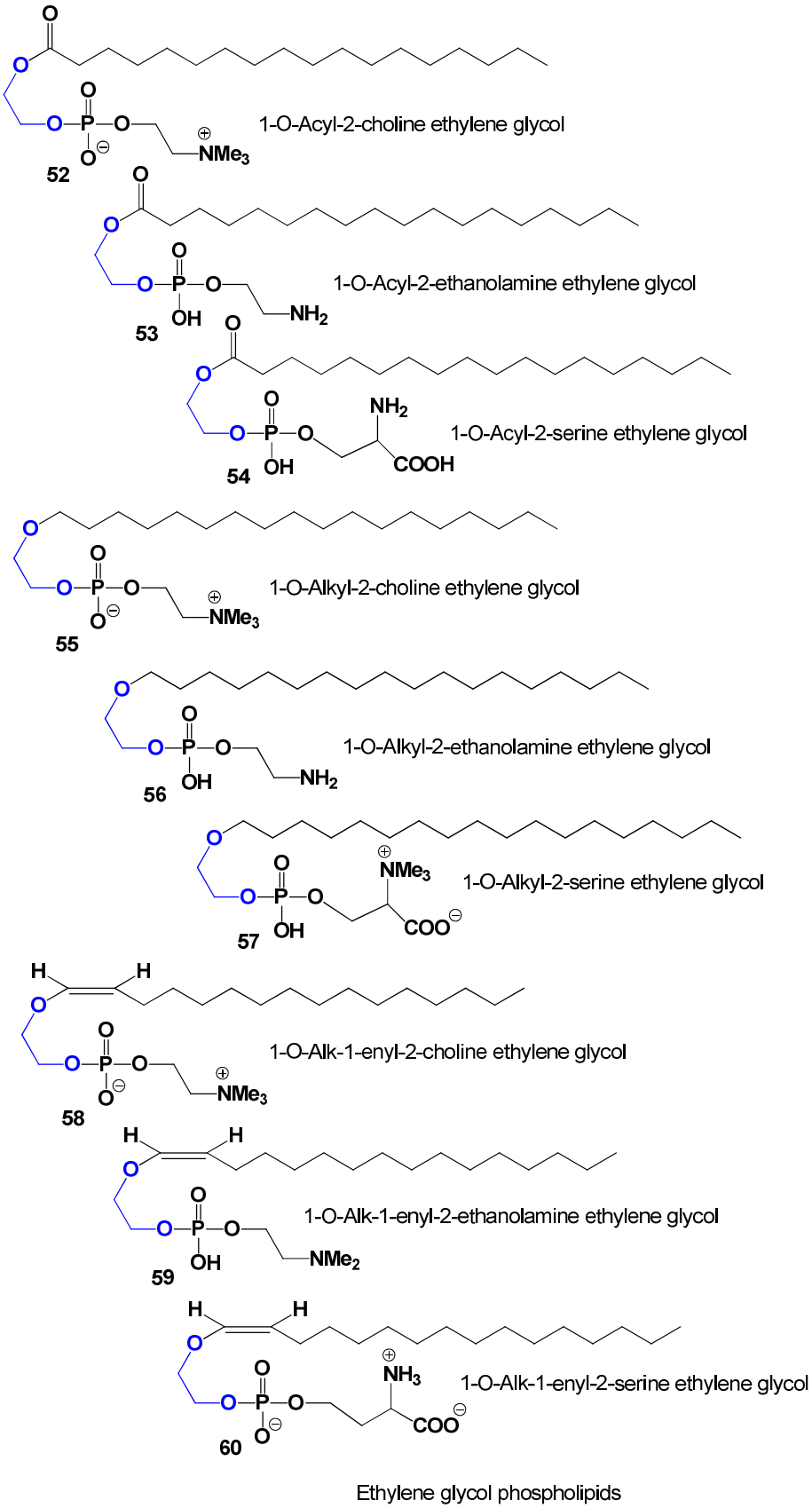

Figure 11. Polar diol phospholipids derived from marine and terrestrial organisms.

Рис. 11. Фосфолипиды полярных диолов, полученные из морских и наземных организмов.

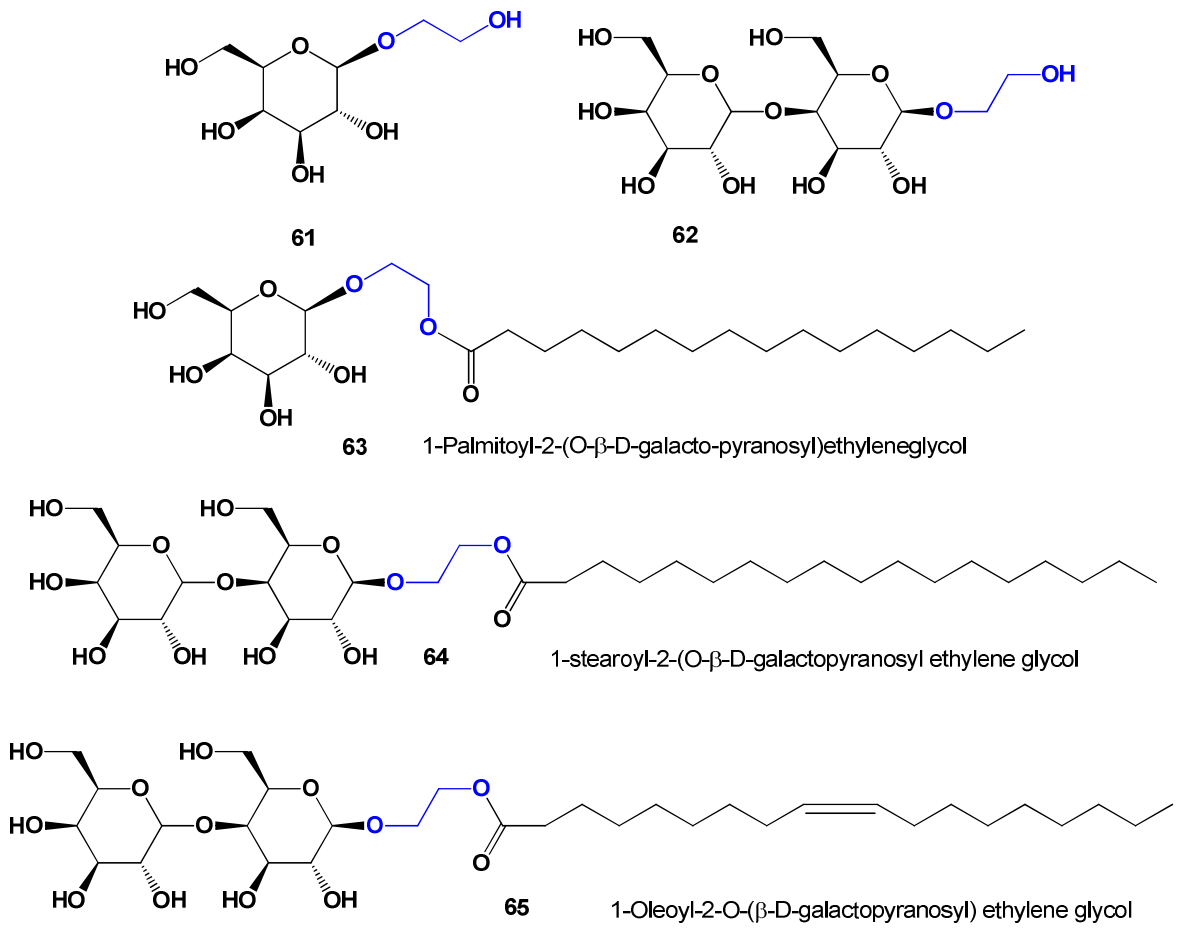

Figure 12. Polar diol glycolipids derived from plants.

Рис. 12. Полярные диольные гликолипиды, полученные из растений.

Biological membranes of the eubacteria, fungi, protist, plantae and animalia are characterized by neutral lipids (**70**-**72**, see **Fig. 14**) and the like, glycolipids (**75**-**77**) and the like, and phospholipids (**80**-**82**) and the like. All these lipids are characterized by the position of acyl chains in positions *sn*-1 and *sn*-2 of glycerol skeletons of neutral, glyco- and phospholipids in Fisher projections, while lipids of the Archaea are characterized by the position of alkyl chains in positions *sn*-2 and *sn*-3 of glycerol skeletons of neutral (**73** and **74**), glyco- (**78** and **79**) and phospholipids (**83** and **84**) [1, 93, 139-145].

It would be interesting to know the ratio of different polyols in protomembranes and biological membranes. According to the mathematical model, the ratio of polyols in the protomembrane (as indicated in **Table 1**) was that ethylene glycol 40%, glycerol – 33%, and butane-1,2,3,4-tetraols – 17%, although in biological membranes the ratio of these polyols other. Glycerol appears to make up over 90 percent of complex lipids, there is no data on ethylene glycol and butane-1,2,3,4-tetraols in complex lipids, but it is still estimated to be between 1 and 3 percent.

Ether lipids, which are the main structural molecules of all Archaea and their possible transformation, have been discussed previously [1] and are not intended to be discussed in this article.

An interesting question is why did glycerol replace ethylene glycol as the main polyol in complex lipids? The question is complex, but it can be said for sure that the physical and chemical characteristics of, for example, diol palmitoylphosphatidylcholine and glycerol dipalmitoylphosphatidylcholine are different. So melting point, solubility, viscosity, surface tension, and other parame-

ters are different. And if many of the listed chemical and physical properties for glycerol dipalmitoylphosphatidylcholine can be found in the scientific literature, then the same properties for the diol palmitoylphosphatidylcholine are not in the literature. Therefore, it is difficult to make comparative characteristics for these two phospholipids. But logic suggests that diol phospholipids have been replaced by their glycerol counterparts apparently already in living organisms.

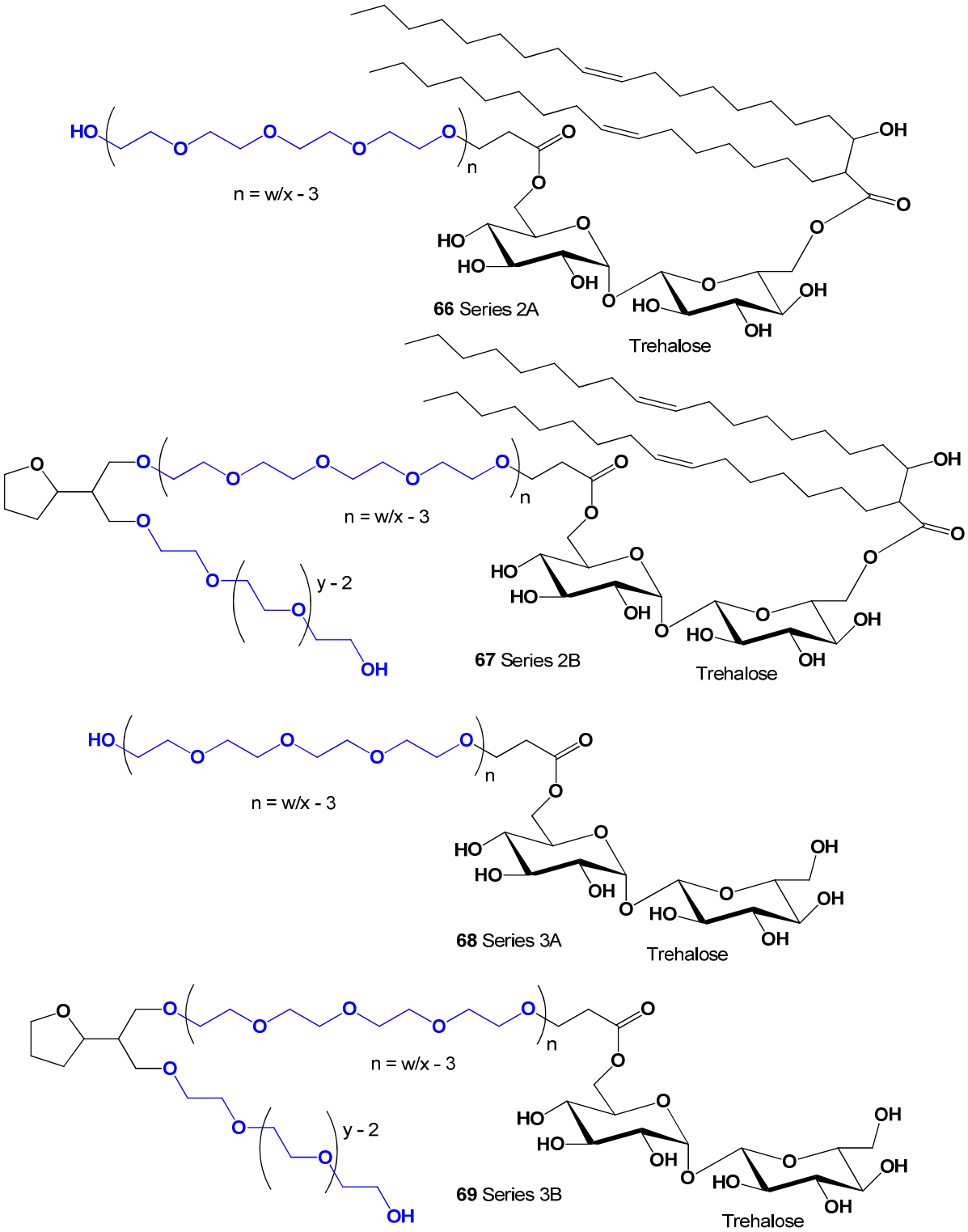

Figure 13. Ethylene glycol glycolipids derived from mycobacteria.

Рис. 13. Гликолипиды этиленгликоля, полученные из микобактерий.

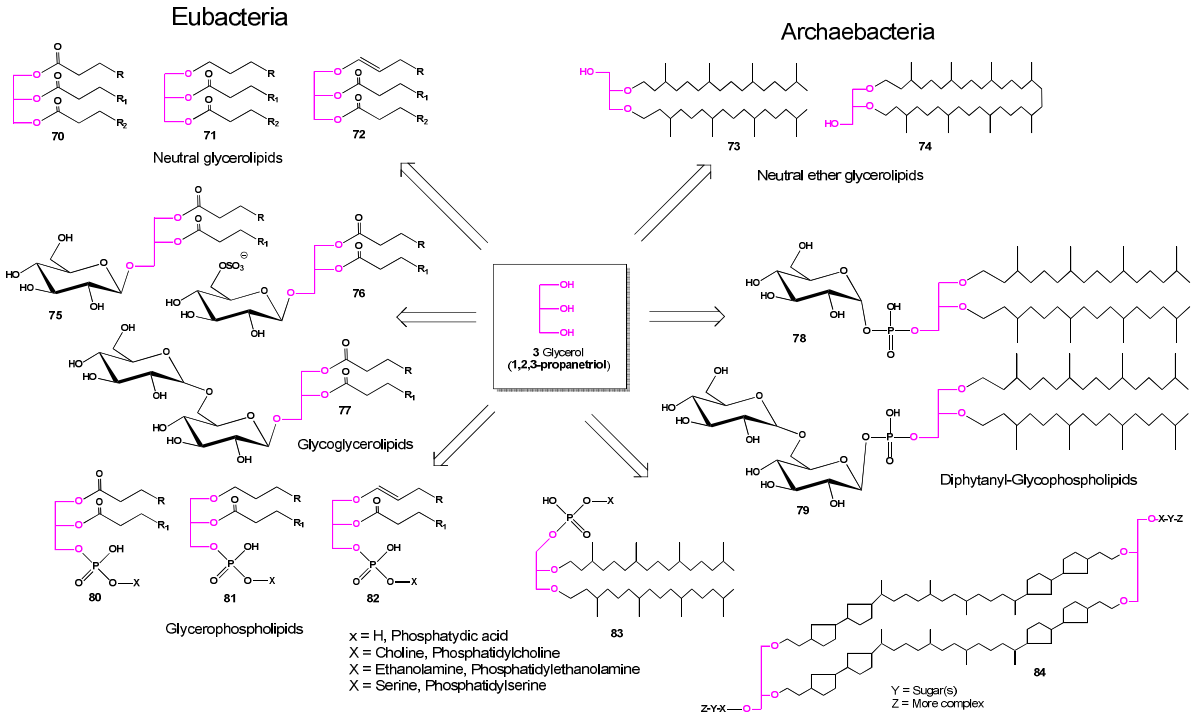

Figure 14. Glycerol (or propane-1,2,3-triol), which is the backbone of all glycerolipids that make up more than 90 percent of the neutral, glyco- and phospholipids of eubacteria and Archaea.

Рис. 14. Глицерин (или пропан-1,2,3-триол), являющийся основой всех глицеролипидов, составляющих более 90% нейтральных, глико- и фосфолипидов эубактерий и архей.

8. Butane-1,2,3,4-tetraols and their distribution in nature

Complex lipids based on butane-1,2,3,4-tetraols are well known in science. These lipids are part of biological membranes, and they probably could have been part of primary coacervates or other pseudo-living formations in the distant years of chemical evolution. The mathematical model allows us to assume that these lipids were and accounted for approximately seventeen percent of the total of all polyols.

Erythritol (**85**, structures are shown in **Fig. 15**) was first isolated from the green alga *Protococcus vulgaris* (family Chlamydo-monadaceae, now known as *Apatococcus lobatus*) in 1852 by C.-A. Lamy who named the substance phycit [146], and later in 1900, erythritol was also isolated from green algae *Trentepohlia jolithus* (family Tren-tepohliaceae) [147]. U. Karsten and collaborators from the University of Rostock (Germany) conducted extensive research on the content of polynols in various types of green algae belonging to the class Trebouxiophyceae and showed that the alga *Apatococcus lobatus* from Austria, Germany and Japan contained erythritol in varying amounts, as well as ribitol [148].

It is known that some red algae such as *Gelidium* and *Gracilaria* occupy a leading position in the world agar trade. However, in addition to agar, they can also be producers of polyols such as glycerol (**3**), erythritol (**85**), threitol (**86**), arabitol, mannitol, sorbitol and dulcitol [149, 150].

Erythritol is a low-calorie flavor enhancer discovered in 1848 by J. Stenhouse from lichen of the genus *Roccella* [151], and more recently, Vietnamese scientists isolated erythritol derivatives (**87-91** and **94**, structures are shown in **Fig. 16**) from lichen *Roccella montagnei* [152]. Erythritol and threitol have also been found in the extracts of the lichen genera *Aspicilia, Dendrographa, Parmelia*, and *Rocella*, and it is produced by the Ascomycetous fungi *Aspergillus*, *Penicillium*, and *Ustilago* [153]. Erythritol in pears and melons is a sugar alcohol made from simple sugars derived from plant starches, which is identical to an ingredient found in nature. In the 1970s, this alcohol was commercialized in Japan and has since been

widely used in many countries around the world [154].

It is known that a L-threitol can accumulate in the tissues of plant leaves and is synthesized from L-sorbose [155]. In addition, erythrite was found in the algae *Protococcus vulgaris* and in filamentous chlorophyte green algae *Trentepohlia jolithus* [156].

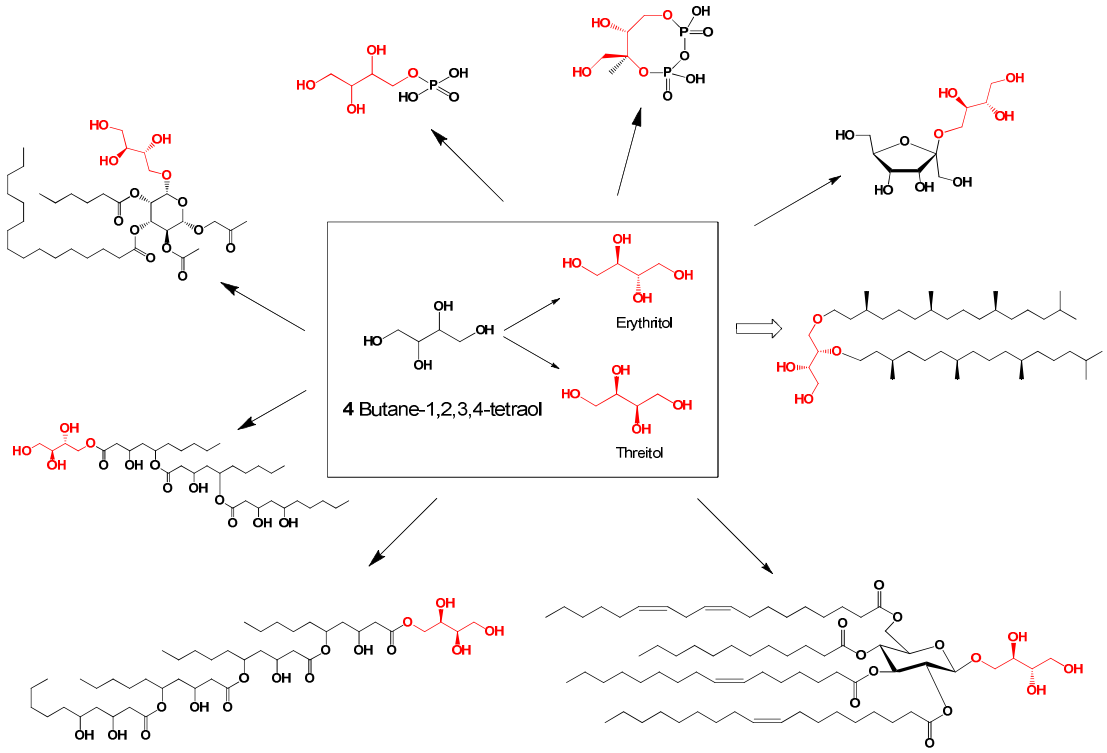

Figure 15. The two main butane-1,2,3,4-tetraols are widespread in nature.
These polyols are the structural building blocks of lipids in biological membranes of Archaea, and, apparently, of some fungi and algae.

Рис. 15. Два основных бутан-1,2,3,4-тетраола широко распространены в природе.

The fungus *Sarcosphaera crassa* called "*Kulak, Göbek kulağı, Çanak*" belonging to the Pezizaceae family from Turkey produces butane-1,2,3,4-tetraol (**4**) and hexane-1,2,3,4,5,6-hexaol [157]. Sugar alcohol (**4**) was isolated from various species of fungi, thus Julius Zellner (1869–1935) in 1910 found it in the pathogenic fungus *Ustilago maydis* spores, Albert Edward Oxford (1822-1900) and Harold Raistrick (1890–1971) in 1935 led it from the mycelium *Penicillium brevicompactum* and *P. cyclopium* [158]. Frank Harold Stodola (1905–1992) in 1946 found it in soil *Aspergillus terreus* [159], also known as *A. terrestris* extract, and J.H. Birkinshaw (1894 – ?) and co-workers in 1948 found that the wood-rotting fungi *Armillaria mellea* produces both the D-threitol and L-erythritol alcohols [160]. Ludwika Tomaszewska (y. b. 1985) and co-workers have shown that erythritol and mannitol produces by *Yarrowia lipolytica* yeast [161].

2-C-methyl-D-erythritol is widely known and distributed in nature, and secondary metabolites, 2-C-methyl-D-erythritol glycosides (**92**-**100**) were isolated from various species of Umbelliferous and Rubiaceae plants [162, 163]. The 2-C-methyl-D-erythritol phosphates (**101** and **102**) have also been isolated from bacteria [164-168], and erythritol phosphate (**103**) is synthesized by Gram-negative bacteria [169, 170].

A series of mannosylerythritol lipids (**104**, one sample) are surface-active compounds that belong to the class of glycolipids of biosurfactants that were isolated from ustilaginomycetous anamorphic yeasts belonging to the genus *Pseudozyma* sp. as the main lipid component, while a heterothallic fungus *Ustilago* sp. produces them as secondary lipids [171].

Maltosyl-erythritol (**105**) is an interesting sugar containing bound erythritol isolated from *Bacillus stearothermophilus* and *Bacillus*

mutanolyticus YU5215, and its structure was determined, and its physicochemical properties studied [172, 173]. Lipids and other metabolites containing erythrite were isolated from various natural sources from the environment shown in **Fig. 11**.

Uncommon and rare a tetritol-diphytanyl-diether (**106**, structure is shown in **Fig. 17**) in which the a- and b- OH groups of the tetritol form ether linkages with two C20 isopranoid alcohols and found in biological membranes of prokaryotes [141, 142, 174, 175].

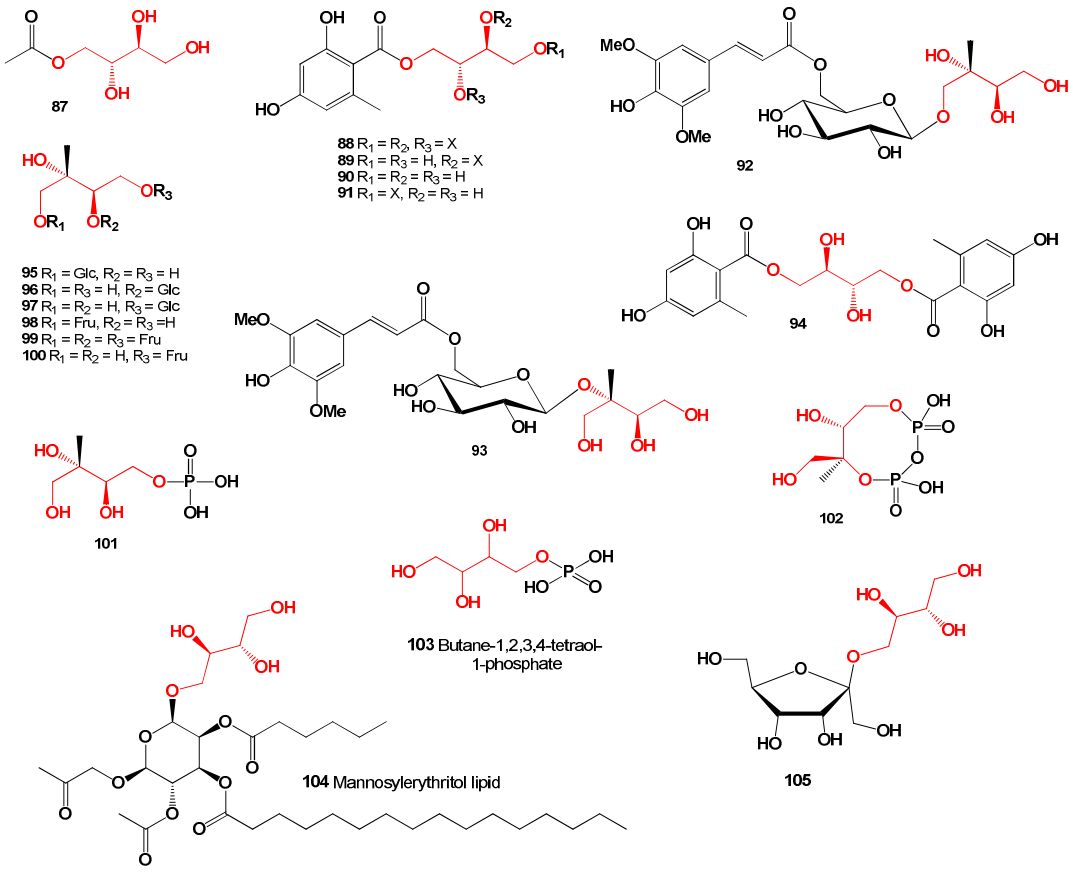

Figure 16. Samples of lipids and other secondary metabolites containing erythrite and/or threitol (butane-1,2,3,4-tetraols) isolated from natural sources.

Рис. 16. Образцы липидов и других вторичных метаболитов, содержащих эритрит и/или треитол (бутан-1,2,3,4-тетраолы), выделенные из природных источников.

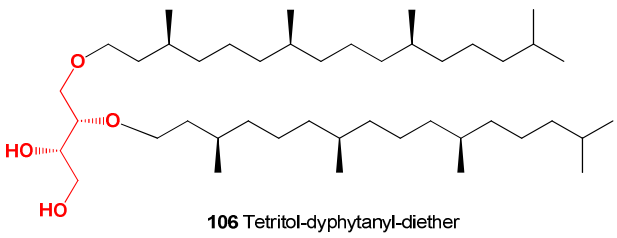

Figure 17. Minor unusual lipid found in extracts of the lipids of Archaea.

Рис. 17. Минорный липид, обнаруженный в экстрактах липидов архей.

Mannosyl-erythritol lipids (MEL, **107-114**, structures are shown in **Fig. 18**) are glycolipids

belonging to the class of biosurfactants. MEL glycolipids are produced by *Pseudozyma* spp. as major lipid components, while *Ustilago* spp. produce them as minor metabolites. MEL glycolipids have been discovered more than six decades ago, but they have recently returned due to their ecological compatibility, as well as their mild production conditions, their chemical structural diversity, and versatile biochemical functions [176-182]. MELs are produced by microorganisms, and they were isolated as oily compounds in a cultured suspension of *Ustilago maydis* PRL-627 [176, 183]. First in 1970, Bhattacharjee and co-workers characterized MEL as a glycolipid and studied the composition of fatty acids, which were represented by acids C12:0, C14:0, C14:1, C16:0, C16:1, C18:0 and C18:1 [184].

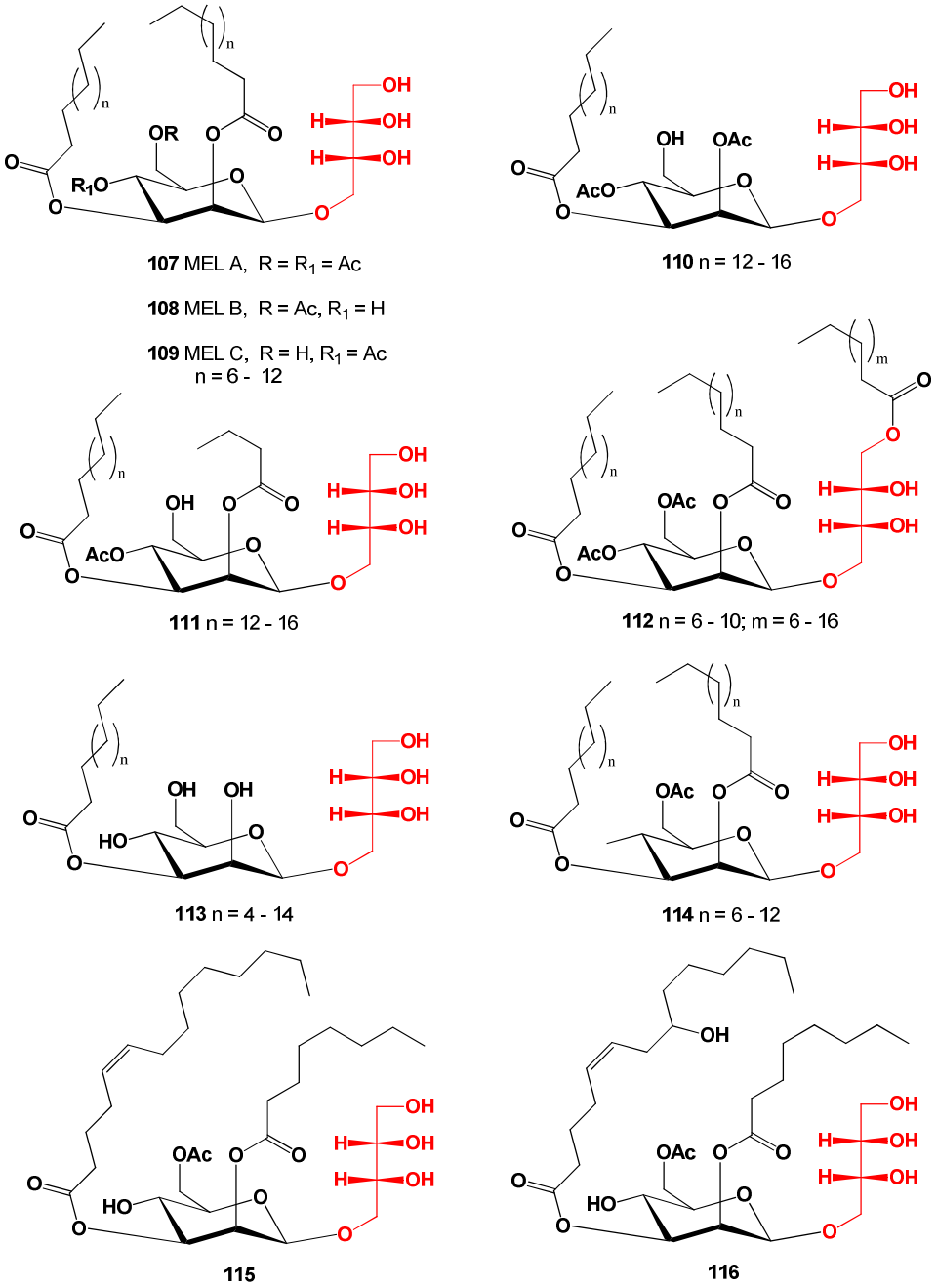

Figure 18. Biosurfactants called mannosylerythritol lipids are produced by Moesziomyces.

Рис. 18. Биосурфактанты, называемые липидами маннозилэритрита, вырабатываются Moesziomyces.

MEL-A, B and C glycolipids have been isolated from many microorganisms and differ in their fatty acid composition. Thus, *Ustilago maydis* DSM 4500 and ATCC 1482 produced 4-O-β-D-mannopyranosyl-D-erythritol (MEL-A) with a set of fatty acids: C14:1 (43%), C6:0 (20%) and C16:1 (12%), and *Candida* SY16 produces MEL-A (**107**) with a set of fatty acids: C6:0, C12:0, C14:0, and C14:1. Mannosylerythritol (MEL-A) with basic fatty acids C10:0, C10:1, and C8:0 was isolated from *Pseudozyma aphidis* DSM 70725 [84] and *Pseudozyma rugulosa* NBRC 10877 synthesizes MEL-A with basic fatty acids, C8:0 (28%), C10:0 (21%) and C10:1 (23%) [185-188].

Mixtures MEL-A (**107**) and MEL-B (**108**) were isolated from *Schizonella melanogramma* with a fatty acid composition C14:0, C16:1, C16:0, C18:0, C18:1, and from *Pseudozyma antarctica* T-34 with a fatty acid composition C8:0 (27%), C10:0 (21%) and C10:1 (27%), respectively [189-191].

MEL-C (**109**) was isolated from *Pseudozyma hubeiensis* KM-59 with acids C6:0, C12:0 and C16:0, *Pseudozyma shaxiensis* with acids C16:0, C16:1, C16:2, and C14:1 and *Pseudozyma graminicola* CBS 10092 with acids C6:0, C8:0, C12:0, C12:1, C14:0, and C14:1 [191-195]. Other MEL glycolipids (**110-114**) with a different set of fatty acids were isolated from microorganisms belonging to the genus *Pseudozyma* [177, 178, 183].

Monounsaturated fatty acids have been identified in a mono-acetylated MEL-B (**115**) and 1-O-β-(2′-O-alka(e)noyl-3′-O-hydroxyalka(e)noyl-6′-O-acetyl-D-mannopyranosyl)-D-erythritol (**116**) which were found in olive and castor oil, respectively. These glycolipids synthesized by the ustilaginaceous yeast-like species, *Pseudozyma tsukubaensis* NBRC1940 [196].

If the fungus *Aureobasidium pullulans* NRRL 50380 uses erythritol or threitol as a substrate, then the produced liamocins contain these polyols combined with a fatty acid and have selective antibacterial activity against *Streptococcus* species. Structural variants of liamocins (**117-120**, structures are shown in **Fig. 19**) represent new antibacterial agents against *Streptococcus* sp. [197].

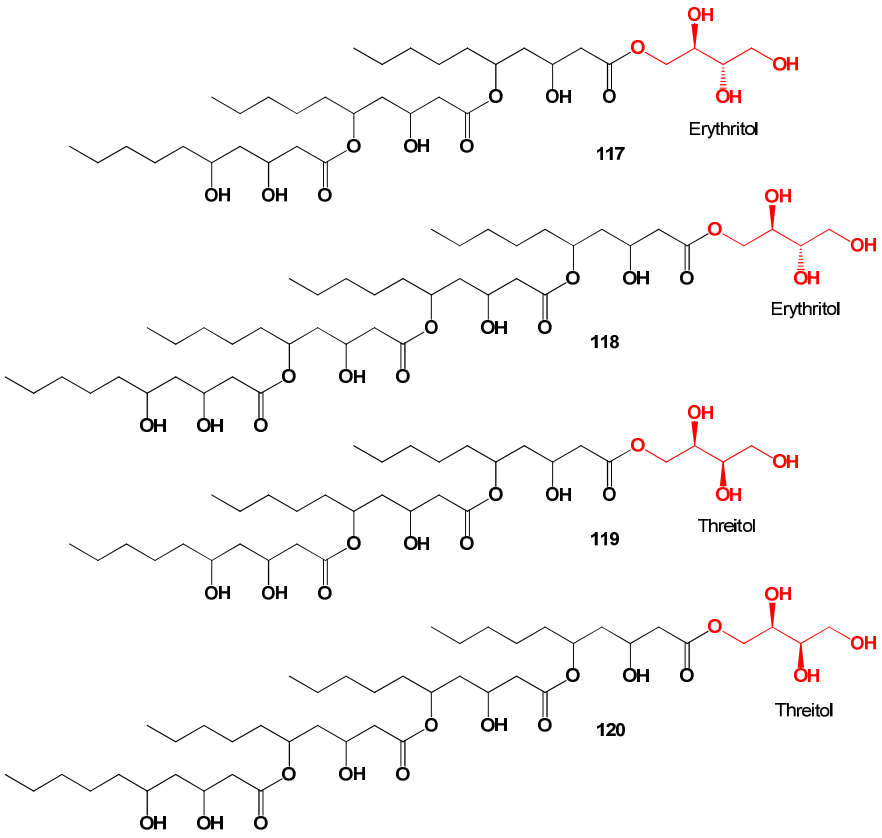

Figure 19. Liamocins produced by the fungus *Aureobasidium pullulans* NRRL 50380 uses erythritol or threitol as a substrate.

Рис. 19. Лиамоцины, продуцируемые грибком *Aureobasidium pullulans*.
В NRRL 50380 в качестве субстрата используется эритрит или треитол.

Unusual erythritol- and mannose-containing glycolipids (**121-125**, structures are shown in **Fig. 20**) have been found in the intracellular lipids of a strain of the com smut pathogenic fungus, *Ustilago maydis*. It is proposed that the major glycolipid component has the structure 4-O-(2,3,4,6-tetra-O-acyl-D-mannopyranosyl)-D-ery-thritol. The fatty acid constituents were found to range from C12 to C18 with the C16 acids predominating [198].

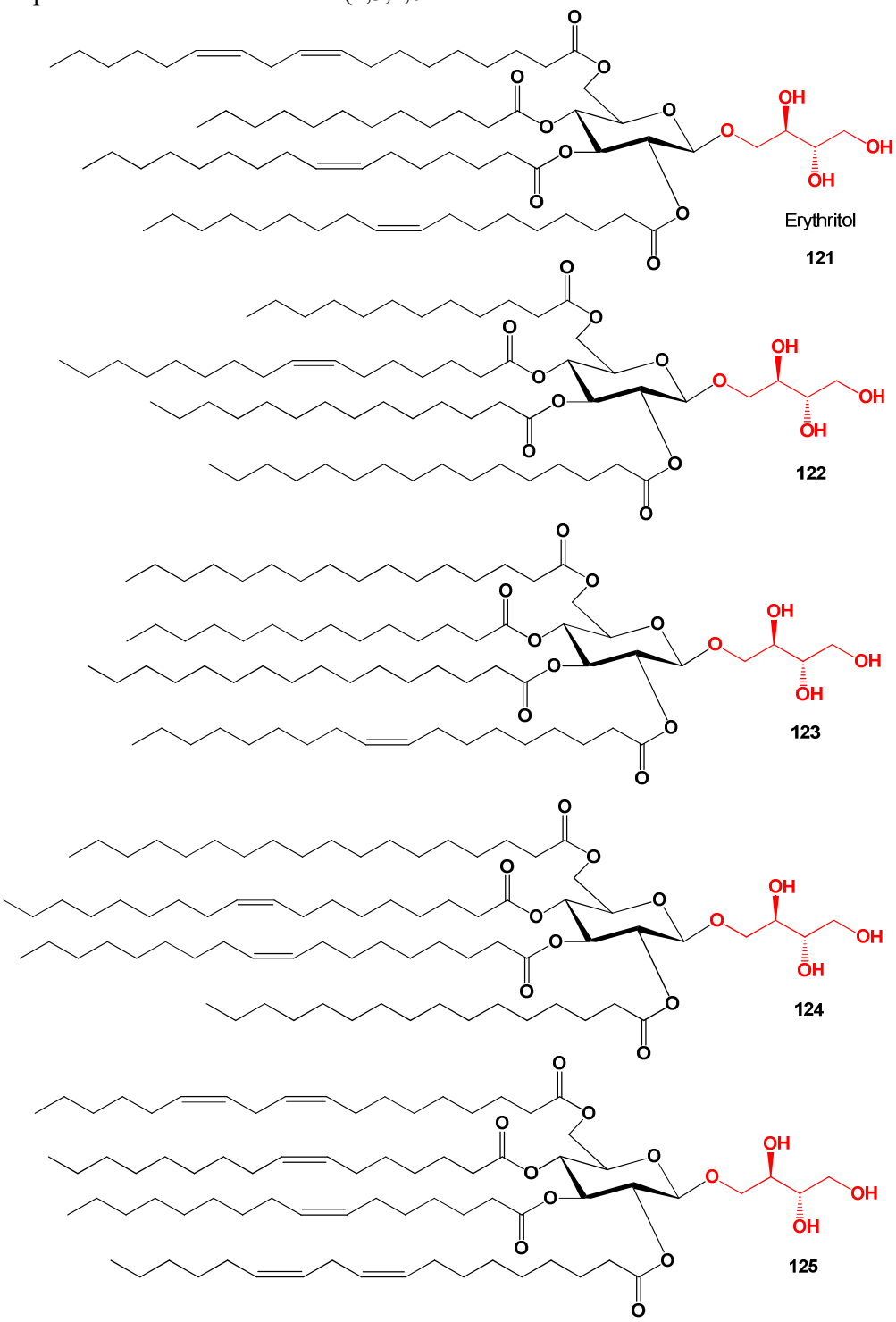

Figure 20. Unusual erythritol- and mannose-containing glycolipids have been isolated from the pathogenic fungus, *Ustilago maydis.*

Рис. 20. Необычные гликолипиды, содержащие эритрит и маннозу, были выделены из патогенного грибка *Ustilago maydis*.

9. Pentane-1,2,3,4,5-pentaols and their distribution in nature

Complex lipids based on pentane-1,2,3,4,5-pentaols are produced by various types of bacteria, and their content of total lipid molecules, according to the mathematical model, does not exceed seven percent. If bacteria retained these lipids, then primitive organisms could probably have them as well.

Sugar alcohols containing five hydroxyl groups and having the common name pentane-1,2,3,4,5-pentols (**5**) are widely present in nature, and the most famous of them are ribitol (**126**, structures are shown in **Fig. 21**), xytitol (**127**) and arabitol (**128**) [199].

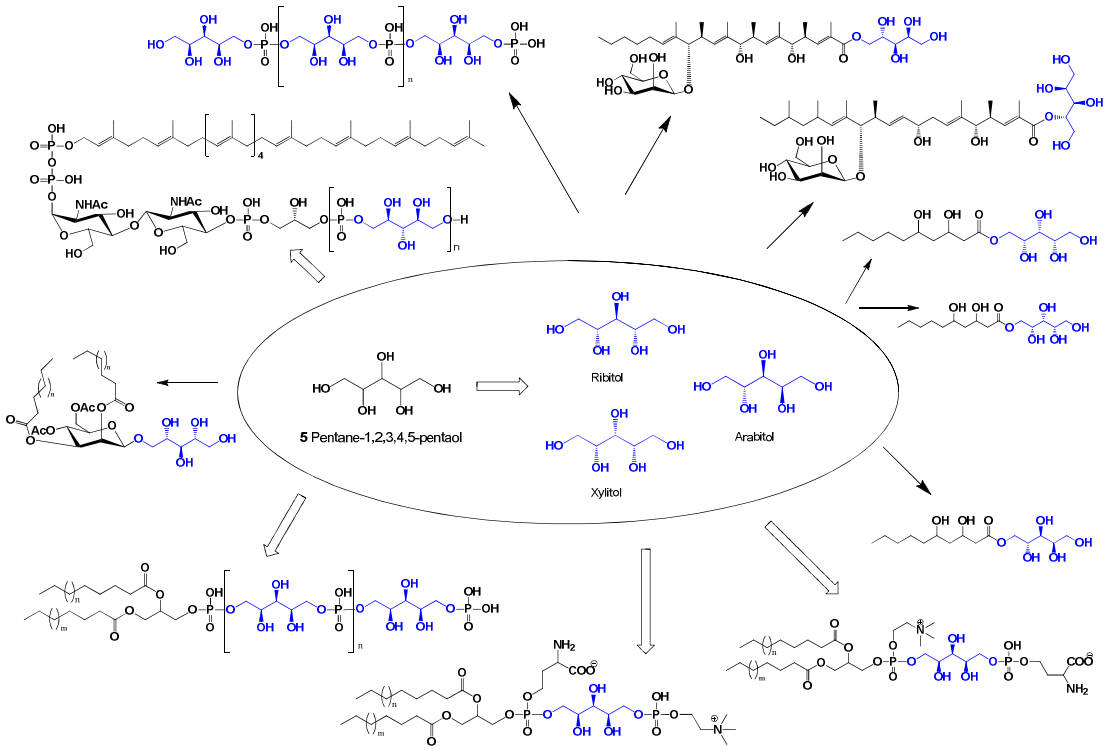

Figure 21. Pentane-1,2,3,4,5-pentols are widely present in nature, and the most famous of them are ribitol, xytitol and arabitol.

These polyols are the structural building blocks of lipids in the biological membranes of eubacteria. All Gram-positive eubacteria, except for micrococci, streptococci, yeast, and filamentous fungi, contain teichoic acids in the cytoplasmic membrane.

Рис. 21. Пентан-1,2,3,4,5-пентолы широко распространены в природе, и наиболее известными из них являются рибит, кситит и арабитол.

Эти полиолы являются структурными строительными блоками липидов в биологических мембранах эубактерий. Все грамположительные эубактерии, кроме микрококков, стрептококков, дрожжей и мицелиальных грибов, содержат в цитоплазматической мембране тейхоевые кислоты.

Ribitol also often called adonitol was first isolated from the leaves of *Adonis vernalis* by Merck in 1893 [200], and its content in the leaves of *Adonis* can vary from 0.9 to 5.3% of dry weight depending on the type of plant [201, 202]. In addition, adonitol has also been found among the active ingredients of *Adonis annua* [203], in the butanolic fraction of the ethanol extract of the roots of *Bupleurum gibraltaricum* and *Bupleurum spinosum* [204], and in the flowers of *Sarcococca coriacea* [205]. Along with glycerol, ribitol is one of the main components of biological membranes in *Bacillus subtilis*, and other Gram-positive bacteria and is part of ribitol teichoic acids, in which their content can reach 50% of the dry weight cell walls [206-211].

The second alcohol containing five hydroxyl groups is xylitol which is found in almost all pastures, as well as in lichens, algae, and yeast. As Von K. Kratzl и H. Silbernagel described, they first

discovered xylitol in mushrooms more than 100 years ago. The production of xylitol by extraction from its natural sources is impractical and uneconomical due to the relatively small quantities in which it occurs, therefore it is customary to obtain it either by synthesis or using biotechnological processes. Among microorganisms, yeast are the best producers of xylitol, especially those belonging to the genus *Candida* [212-215].

The third alcohol, which contains five hydroxyl groups, is called arabitol, also it can be called arabinitol or xylitol was found in lichens *Roccellia lonica*, *Xanthoria aureola*, *Parmelia conspersa* and other species [216-218]. It is known that lichens are complex organisms containing microalgae and fungi, which represent a symbiotic partnership of two separate organisms. The dominant partner is the fungus, which gives the lichen most of its fungal characteristics [216,217]. Lichens contain a wide variety of metabolites that are produced by both the fungus and the symbiotic alga [218-229]. The third alcohol, which contains five hydroxyl groups, is called arabitol, also it can be called arabinitol or xylitol was found in lichens *Roccellia lonica*, *Xanthoria aureola*, *Parmelia conspersa* and other species [230-233].

It is known that osmophilic yeasts accumulate various polyols under the influence of many environmental factors, and arabitol is one of such polyols that prevents yeast degradation. Some types of yeast such as the genera *Candida*, *Pichia*, *Debaryomyces* and *Zygosaccharomyces* are used to produce arabitol and gave up to 84 g/L of this alcohol [234].

The distribution of various polyols in 34 species of green algae belonging to the family Trebouxiophyceae was studied and it was shown that the algae *Chloroidium ellipsoideum, C. Saccharophilum, C. angusto-ellipsoideum, Chlorella luteoviridis, C. luteoviridis, Coccomyxa viridis, C. avernensis, C. mucigena, Coccomyxa* sp. and *Apatococcus lobatus* contained free and/ or bound ribitol (**126**) [148]. In addition, green algae such as *Trebouxia glomerata, T. erici, Tolypothrix tenuis*, *Nostoc* species, *Calothrix brevissima, Phormidium angustissimum, Phormidium jadinianum* and *Chlorella elliposidea* also contained ribitol [235]. The symbiotic green algae *Trebouxia* sp. of the lichens *Lasallia pustulata* and *Umbilicaria hirsuta* synthesized ribitol in large quantities [236]. Ribitol (**126**) and arabitol (**127**) have been found in the *Trebouxia* sp. photobiont of several other lichens such as *Hypogymnia physodes, Platismatia glauca* and *Xanthoria aureola* [237, 238].

Sugar alcohol, arabitol (arabinitol) is synthesized by many types of yeast, and they can produce arabitol from various sugars, including arabinose. To date, more than 2,000 yeast species have been studied and the species that synthesize arabitol in the largest quantities from arabinose have been identified. Such species include *Candida tropicalis* NRRL Y-11860, *Pichia stipitis* NRRL Y-7124, *Pichia guilliermondii* NRRL Y-2075, *Debaryomyces hansenii*, and *Rhodotorula mucilaginosa* PTD3. In addition, yeast has been found that it can convert glucose into arabitol. These species include, *Pichia ohmeri* No. 230, *Hansenula polymorpha* DSM 70277, *Metschnikowia reukaufi* AJ14787, *Zygosaccharomyces rouxii* NRRL Y-27624, *Kodamaea ohmeri* NH-9, and *Debaryomyces nepalensis* NCYC 3413 [239-242]. Xylitol is a polyol sugar alcohol called birch sugar because it is found in birch wood and sap, *Betula platyphylla* var. *japonica* [243], and xylitol is found in plums, strawberries, ripe cranberries, raspberries and rowan berries, cauliflower, and pumpkin as well as in lichens, seaweed, and yeast [244-246].

Extracellular lipids such as glycolipids were discovered in several yeasts, bacteria, and filamentous fungi over 50 years ago and are of great interest for their potential biological activity [217, 220, 221, 247-253]. This group includes glycolipids, which also include pentane-1,2,3,4,5-pentols such as ribitol, xytitol and arabitol [254].

A polyketide glycoside called cladionol A (**129**, structures are shown in **Fig. 22**) was isolated from the cultured broth of a fungus *Gliocladium* sp., which was separated from sea grass *Syringodium isoetifolium*, and it exhibited modest cytotoxicity [255].

More recently same polyketide glycoside called bionectriol A (**129**) is produced by a fungal culture of *Bionectria* sp., which was isolated from a fungus garden of the fungus-growing ant *Apterostigma dentigerum* [256]. The closest structural relatives of cladionol A and bionectriol A are roselipins 1A and 1B, which were previously isolated from a marine fungal isolate of *Gliocladium roseum* KF-1040, the anamorph of *B. ochroleuca* [257, 258]. In addition, diastereomeric polyketide glycosides, roselipins 3A-3E (**129**, **130**, **133**, **134** and **135**), have been isolated from the acetone extract of the fungus *Clonostachys candelabrum* (family Bionec-triaceae) with positive anthelmintic activity [259].

Fiehn and co-workers reported that the oleaginous yeast *Rhodotorula babjevae* UCDFST 04-877 produces extracellular lipids with biosurfactant properties (**136-141**, structures are shown in

Fig. 23). D-arabitol appeared as the backbone of these lipids. Using GC-MS, the main components were identified as D-arabitol acetylated (*R*)-3-hydroxymyristate, (*R*)-3-hydroxypalmitate, and (*R*)-3-hydroxystearate [260].

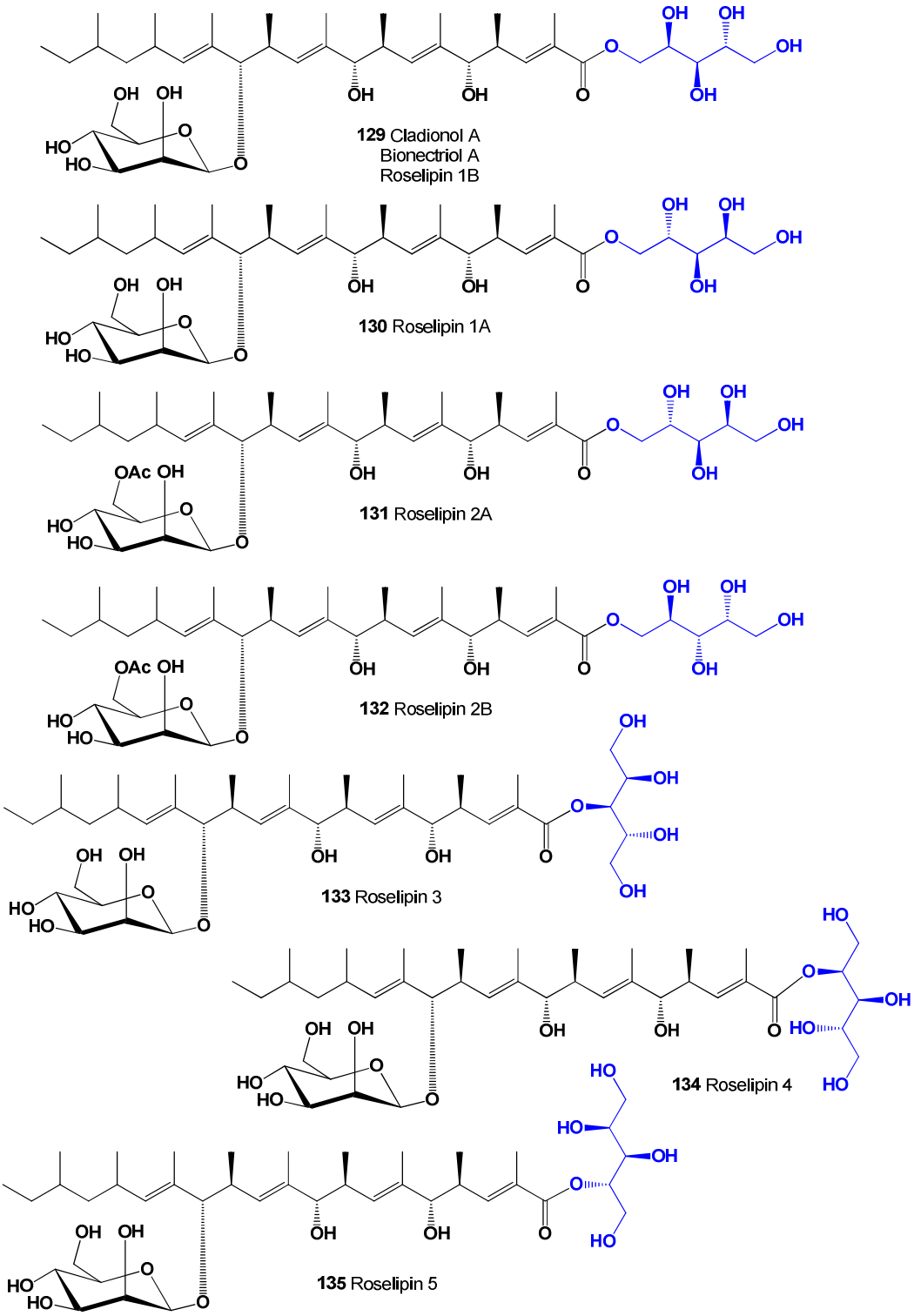

Figure 22. Glycolipids containing pentane-1,2,3,4,5-pentols such as ribitol, xytitol and arabitol are produced by fungi belonging to the genus Hypocreaceae.

Рис. 22. Гликолипиды, содержащие пентан-1,2,3,4,5-пентолы, такие как рибит, кситит и арабитол, продуцируются грибами, принадлежащими к роду Hypocreaceae.

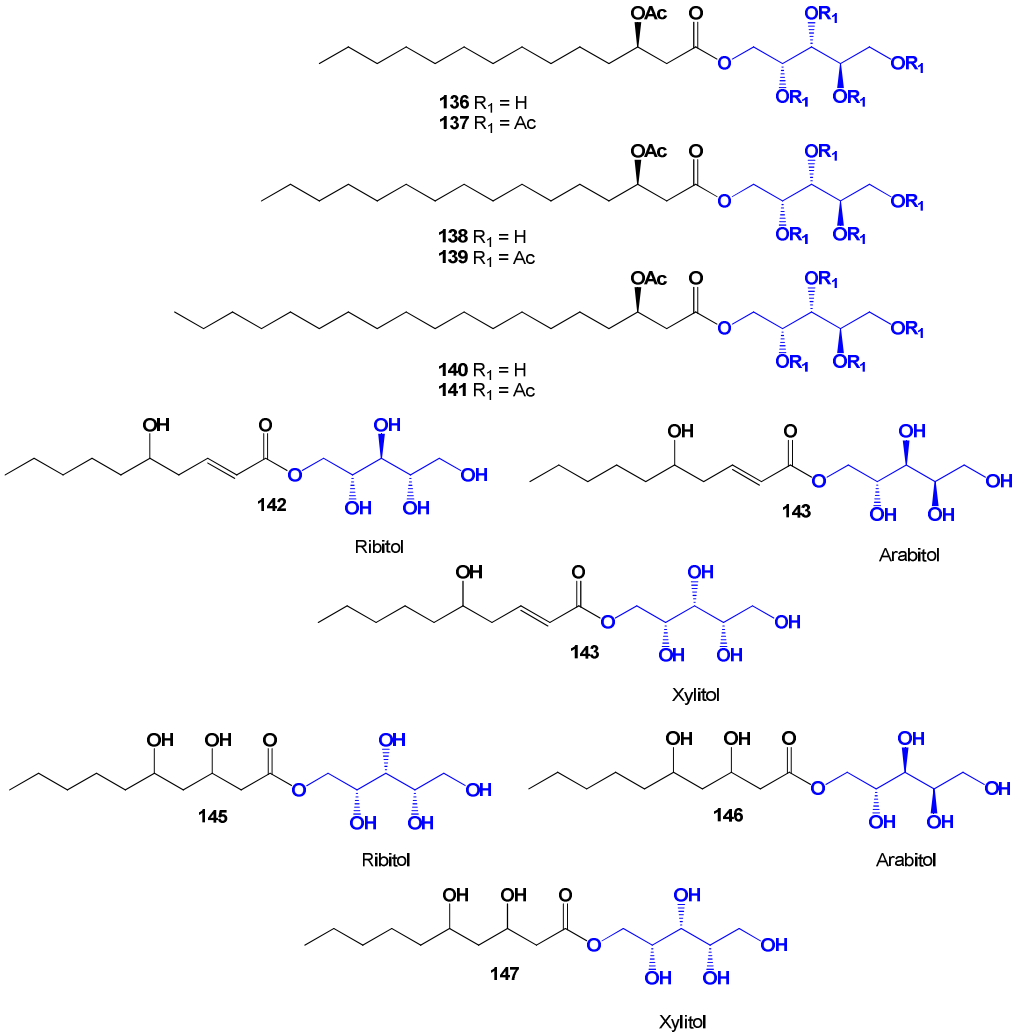

Figure 23. Glycolipids containing pentane-1,2,3,4,5-pentols such as ribitol, xytitol and arabitol.

Рис. 23. Гликолипиды, содержащие пентан-1,2,3,4,5-пентолы, такие как рибит, кситит и арабитол.

A group of lipids called liamocins, which are polyol lipids and are produced by several species of fungi belonging to the Dothioraceae family. These lipids were discovered and first isolated from microorganisms about ten years ago [197, 261]. Many liamocins have selective antibacterial activity against *Streptococcus* species and shown antitumor activity [262]. These lipids are an ester of the D-mannitol head group linked to the acyl chains of 3,5-dihydroxydecanoate, three or four of which are linked together by 1,5-polyether bonds (liamocins Man-A1 and Man-B1) and similar 3'-O-acetylated analogs (Man-A2 and Man-B2). In addition, other types of liamocins are produced depending on the choice of strain and growth conditions. Cultivation of fungi on various sugars leads to significant structural chemical variations, including liamocins with D-galactitol (dulcitol), D-sorbitol (glucitol), ribitol (**142**, **145, 148** and **149**, structures are shown in **Fig. 23** and **24**) D-xylitol (**144, 147**, **152**, **153**, **154** and **155**), D- and L-arabitol (**143, 146**, **156**, **157**, **158** and **159**), L-threitol and glycerol head groups [197, 261, 263-266].

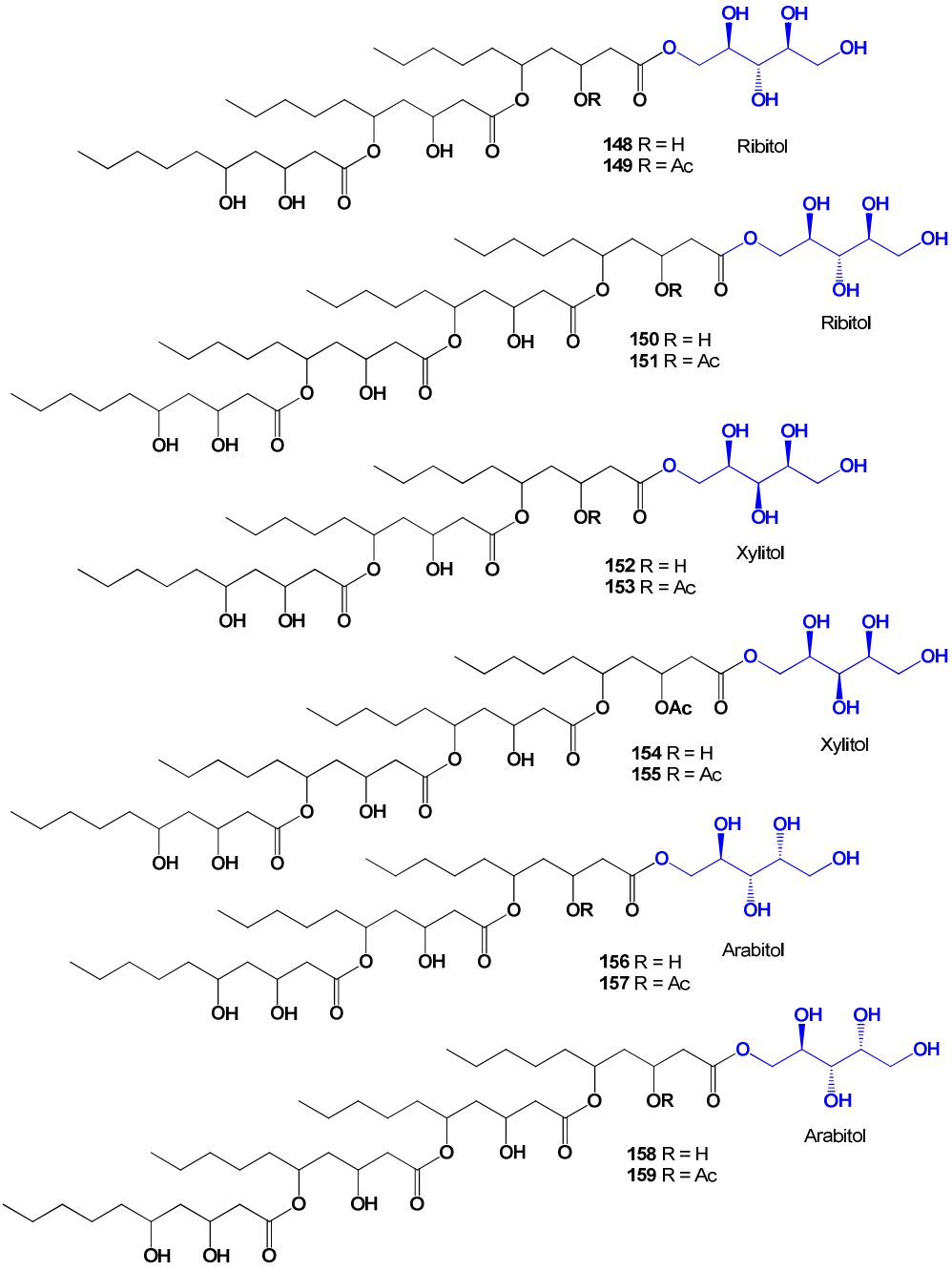

Figure 24. Glycolipids containing pentane-1,2,3,4,5-pentols such as ribitol, xytitol and arabitol produced by fungi from the Dothioraceae family.

Рис. 24. Гликолипиды, содержащие пентан-1,2,3,4,5-пентолы, такие как рибит, кситит и арабитол, продуцируемые грибами семейства Dothioraceae.

All gram-positive eubacteria, except for micrococci and some streptococci, as well as yeast and filamentous fungi, contain teichoic acids in the cytoplasmic membrane area (up to 2% of dry biomass). Teichoic acids were discovered in 1958 by J.J. Armstrong and co-workers to determine the function of CDP-glycerol and CDP-ribitol in *Bacillus subtilis, Lactobacillus arabinosus* and some other bacteria [267]. The term teichoic acid encompasses a diverse family of cell surface glycolpolymers containing repeating polyol units linked by a phosphodiester bond [268]. Teichoic acids include both lipoteichoic acids, which are anchored

in the bacterial membrane through a glycolipid, and wall teichoic acids, which are covalently attached to peptidoglycan. Membrane teichoic acids are predominantly glycerol-phosphate polymers, often associated with glycolipids and phospholipids (lipoteichoic acids). In some microorganisms, only lipoteichoic acids are detected, and free teichoic acids are not [269-271]. Teichoic acids were not found in the membranes of gram-negative bacteria [272].

Ribitol teichoic acids are copolymers of glycerol and/or ribitol phosphate and carbohydrates linked *via* phosphodiester bonds [273-276]. Ribitol teichoic acids are found within the cell wall of most Gram-positive bacteria belonging to the genera *Staphylococcus, Streptococcus, Bacillus, Clostridium, Corynebacterium*, and *Listeria*, which make them potential antibiotic targets for Gram-positive bacteria. In the late 1950s, the constituent fragments of *Bacillus subtilis* and *Lactobacillus arabinosus* walls such as ribitol phosphates (**160**, **161**, **162**, **166**, structures are shown in **Fig. 25**) and ribitol carbohydrate(s) (**163-165**) were first found [267,268,277-280]. Later, the structures of copolymers (**167**) and individual ribitol-glycerol phospholipids (**168** and **169**) were established [281].

Fig. 26 shows the chemical structure of *Staphylococcus aureus* cell wall poly (ribitol phosphate) teichoic acid membrane bound with a prenyl-linked disaccharide. As an example of the distribution of ribitol in nature, we present in Figure 21 the chemical structural model of the ribitol teichoic acid complex (**170**) isolated from the gram-positive human pathogen *Streptococcus pneu-moniae* [282]. Samples of the chemical structures of a complex ribitol teichoic acids (**171-174**) isolated from bacteria are presented in **Fig. 27**.

Cultivating the *Pseudozyma parantarctica* strain on olive oil, D-ribitol, and D-arabitol, it produced mannosyl-D-ribitol lipids (**175**, MDRL-A, structures are shown in **Fig. 28**), mannosyl-L-ribitol lipids (**176,** MDRL-B), mannosyl-D-arabitol lipids (**177**, MDAL-A), mannosyl-D-mannitol lipids (**191**, MML-A), and mannosyl-D-mannitol lipids (**192**, MML-B), respectively [177,183,283], and upon cultivation another strain, *Pseudozyma tsukubaensis*, in a medium containing an excessive amount of optical isomers of D-arabitol, it produced a glycolipid, monoacetylated mannosyl-D-arabitol lipid (**178**, MLAL-B) [177, 183, 283, 284].

10. Hexane-1,2,3,4,5,6-hexaols and their distribution in nature

Hexitols or hexane-1,2,3,4,5,6-hexaols in proto-membranes amounted to no more than two percent, but their content in modern organisms is very small. This suggests that at present this type of lipids is synthesized by some types of bacteria and plants.

Hexitols, sugar alcohols that include mannitol, allitol, galactitol, sorbitol (D-glucitol), galactiol, iditol, and talitol and contain six hydroxyl groups each found in natural sources (**179-184**, structures are shown in **Fig. 29**). The most famous of them is mannitol, which is widely distributed in bacteria, yeasts, fungi, algae, lichens, and several plants like pumpkins, celery, onions, grasses, olives, and mistletoe [285-290].

Mannitol (**179**) is a polyol or six-carbon sugar alcohol and is a stereoisomer of sorbitol. It is suggested that the French chemist Joseph Louis Proust discovered mannitol in 1806 [291]. It was originally isolated from a flowering ash tree and named manna due to its alleged similarity to biblical food [292]. In 1881, Croatian pharmacist and chemist Julije Domac (1853–1928) established the chemical structure of hexene, and mannitol obtained from *Caspian manna*. He determined the position of the double bond in the hexene obtained from mannitol and proved that it is a derivative of normal hexene. Prior to this, the structure of mannitol was unknown [293, 294]. *Caspian manna*, also known as camelthorn, camelthorn-bush, and Persian mannaplant, is a shrub, *Alhagi maurorum*, which grows in a region stretching from the Mediterranean to Russia but has been introduced to many other regions of the world including Australia, southern Africa, and west of the United States [295-297]. Although according to other sources manna, the exudate produced by the manna ash tree *Fraxinus ornus*, was the commercial source for mannitol for many years until the 1920s [298]. The *Fraxinus ornus*, the manna ash or South European flowering ash, is a species of Fraxinus native to southern Europe and southwestern Asia, from Spain and Italy north to Austria and the Czech Republic, and east through the Balkans, Turkey, and western Syria to Lebanon and Armenia [299].

Mannitol has been found in seaweeds such as *Ascophyllum nodosum, Fucus serratus, F. vesiculosus, F. spiralis, Halidrys siliquosa, Himanthalia elongate, Laminaria hyperborean, L. digitate, Pelvetia canaliculate*, and *Saccharina latissimi*, and these types of algae are used for industrial alcohol production [300-302].

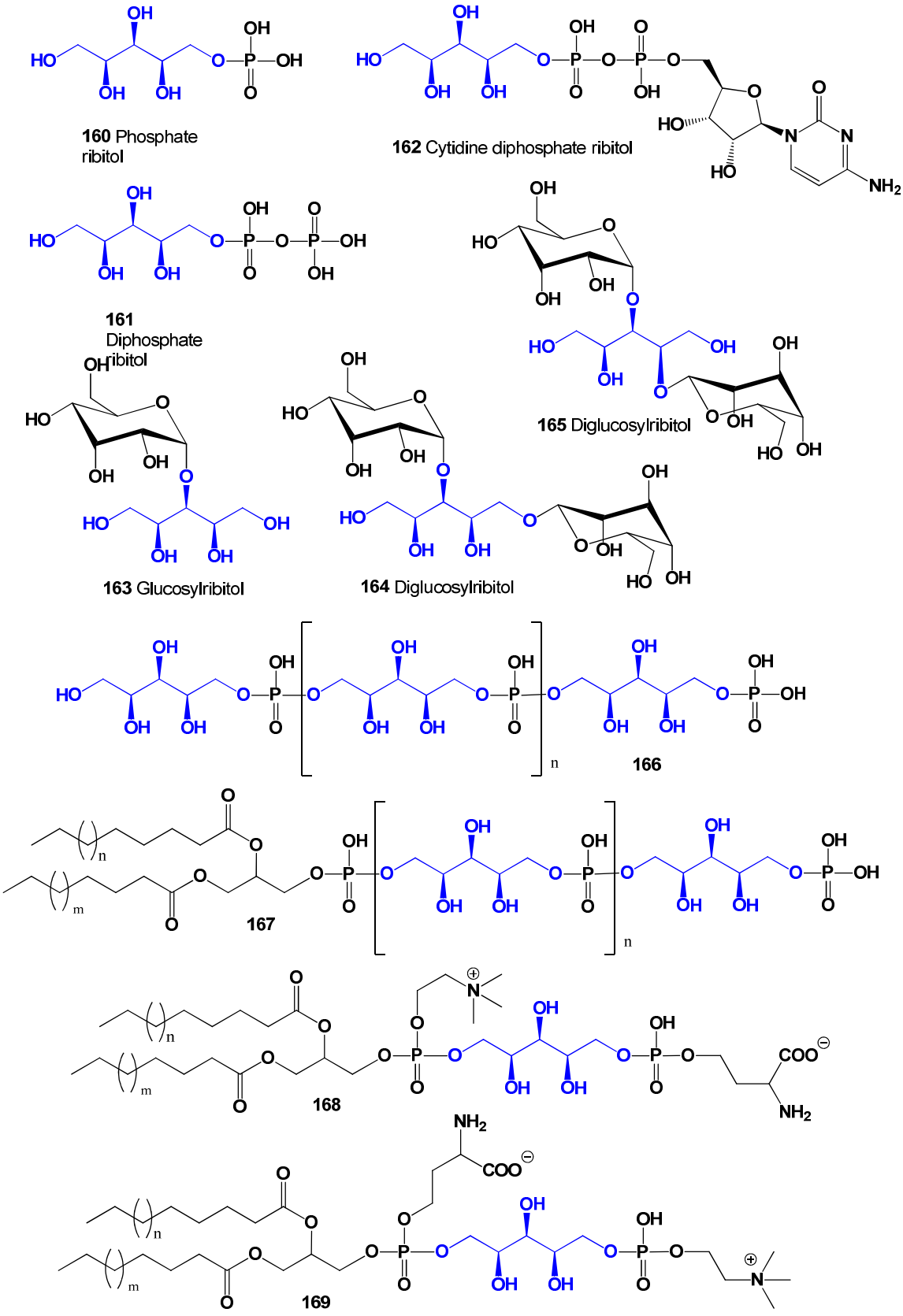

Figure 25. Ribitol teichoic acids derived from the cell wall of most Gram-positive bacteria.

Рис. 25. Рибитол-тейхоевые кислоты, полученные из клеточной стенки большинства грамположительных бактерий.

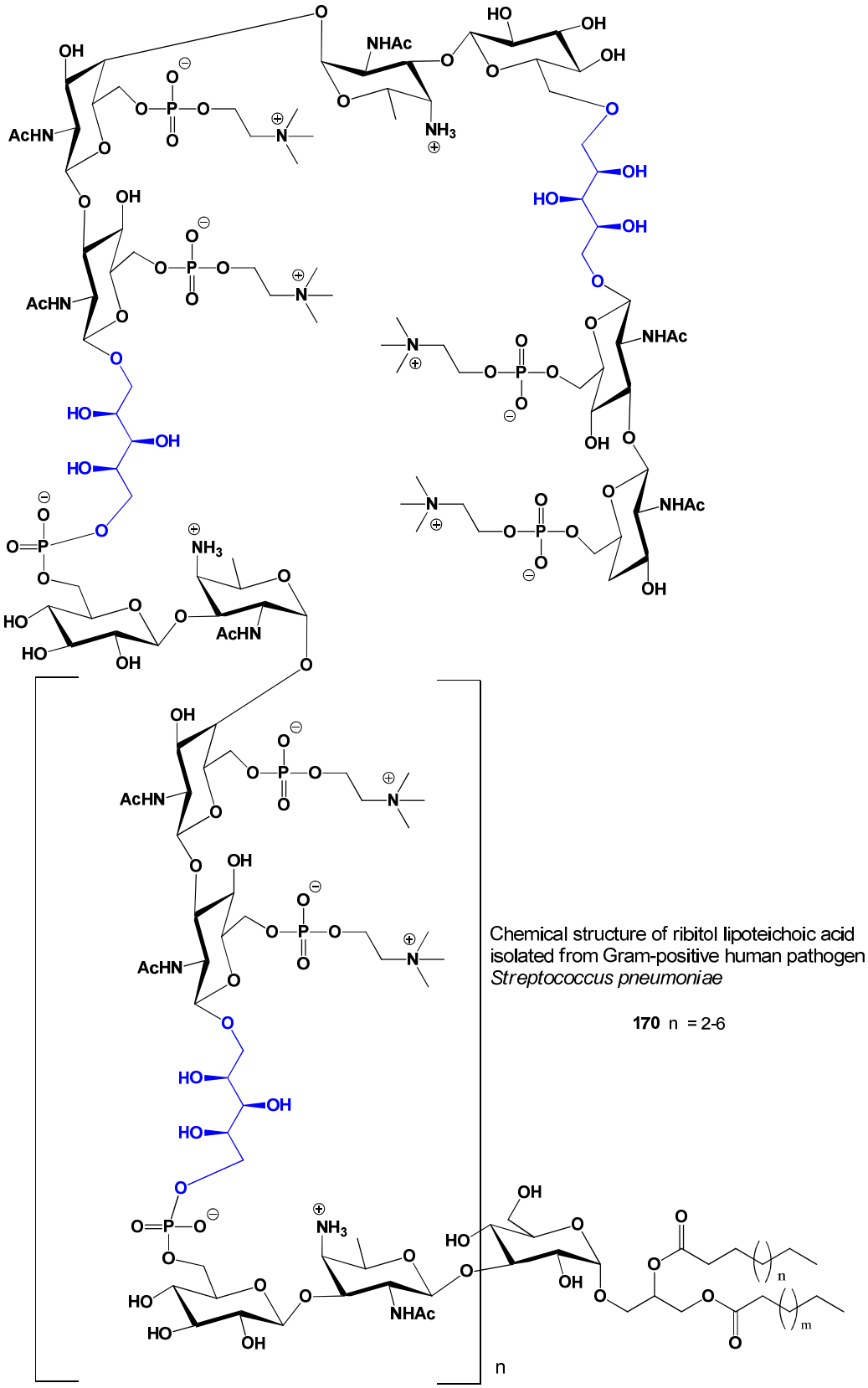

Figure 26. Revised structural model a complex ribitol teichoic acids which isolated from a Gram-positive human pathogen *Streptococcus pneumonie*.

Рис. 26. Пересмотренная структурная модель комплекса рибит-тейхоевых кислот, выделенного из грамположительного возбудителя *Streptococcus pneumonie*.

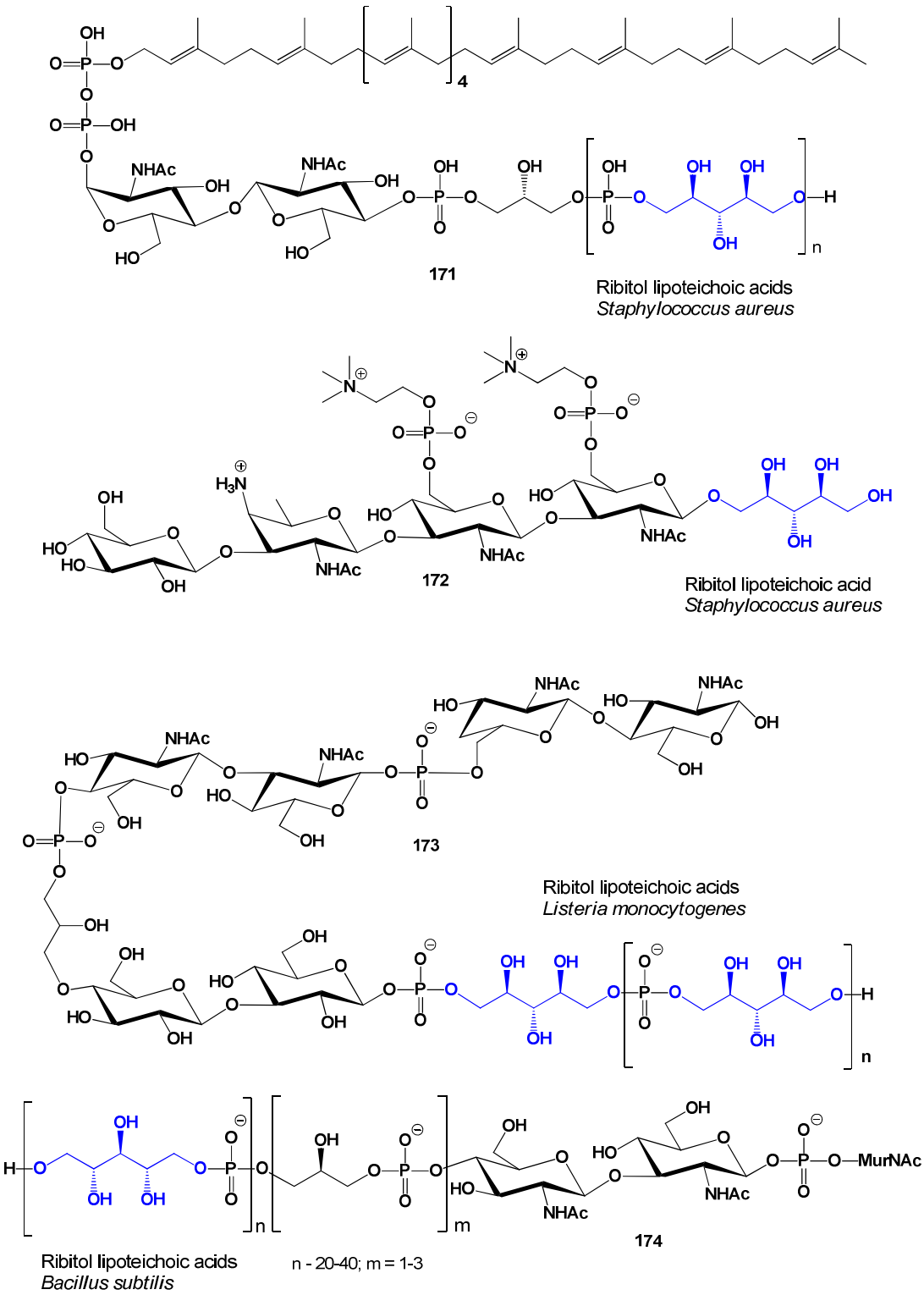

Figure 27. Structure of cell wall teichoic acids from *Staphylococcus aureus, Listeria monocytogenes* and *Bacillus subtilis.*

Wall teichoic acids are anionic polymers of glycerol-phosphate, ribitol-phosphate, and/or glucosyl-phosphate and are tethered to the peptidoglycan.

Рис. 27. Структура тейхоевых кислот клеточных стенок *Staphylococcus aureus, Listeria monocytogenes* и *Bacillus subtilis.*

Тейхоевые кислоты стенки представляют собой анионные полимеры глицерол-фосфата, рибитол-фосфата и/или глюкозил-фосфата и связаны с пептидогликаном.

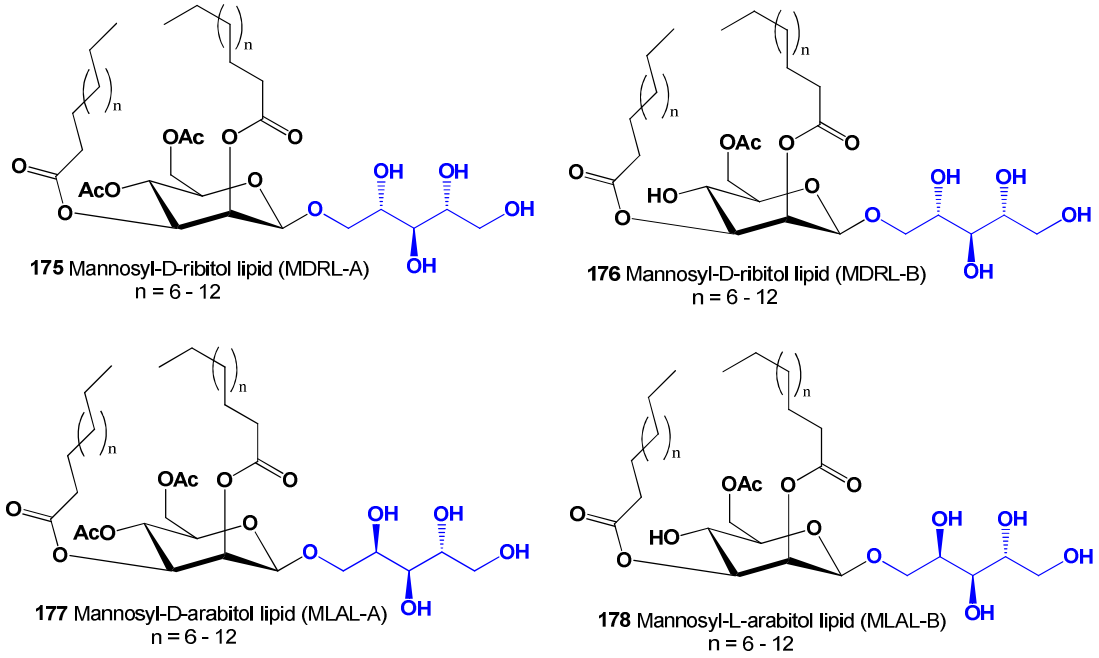

Figure 28. Mannosyl-D- pentane-1,2,3,4,5-pentol glycolipids derived from *Pseudozyma* species.

Рис. 28. Гликолипиды маннозил-D-пентан-1,2,3,4,5-пентола, полученные из видов Pseudozyma.

Mannitol is the main storage carbon in the mushroom, *Agaricus bisporus*, accounting for 50% of the dry body weight of the fruit, and white-spored species of fungus *Aspergillus candidus* can convert up to 50% of the glucose consumed to mannitol [303-305]. In addition, mannitol has also been found in the fungi *Agaricus campestris, Cantharellus cibarius, Cordyceps militaris, Lactarius bertillonii, L. vellereus, Lentinus edodes, Mycoamaranthus cambodgensis, Piloderma croceum, Pleurotus ostreatus, P. tuberregium, Volvariella volvacea, Rhodotus palmatus* and *Xerocomus chrysenteron* [306-314]. Lichens *Evernia prunastri*, *Xanthoria parietina, Cladonia convoluta, C. sandstedei, C. confusa, C. amaurocraea* and some other lichenized Ascomycetes contain mannitol, unusual fatty acids, lipids, and other bioactive metabolites [218-221, 225-229, 315, 316]. There is also information that summarizes data on the content of mannitol in more than 100 species in green plants, fungi, and fungal endophytes [288, 317-319].

Sometimes ago, a new class of glycolipids called polyol fatty acid esters (**185-190**, structures see in **Fig. 30**) has emerged, which is produced by the basidiomycetes of the yeast *Rhodotorula babjevae* [260, 320]. In addition, *Rhodotorula taiwanensis* MD1149 has recently been shown to produce mannitol containing lipids. These lipids are biosurfactants with detergent, antimicrobial, skin moisturizing and emulsifying properties and are widely used on an industrial scale [321].

D-Glucitol (**181**) was found in the fruits of plants of the genera *Cotoneaster, Crataegus, Photinia, Pyrus, Pyracantha, Rosaceae* and *Sorbus* [322]. Allitol (**180**) is a rare sugar alcohol that has various physiological effects, such as laxative effects, to treat constipation and anti-obesity effects by inhibiting lipid accumulation. In addition, allitol cross-links D- and L-hexose, thereby contributing to the production of L-picicose. Allitol is synthesized through microbial (*Klebsiella oxytoca* G4A4) and enzymatic synthesis from D-psychosis and directly from D-fructose [323, 324]. L-Iditol can be obtained from d-sorbitol using for this purpose the resting cell system of methanol yeast, *Candida boidinii* (*Kloeckera* sp. No. 2201) [325]. When D-xylose is disposed of by bacteria, yeast, or fungi, galactitol, sorbitol, and other low molecular weight polyols are formed [326]. It is known that an oleaginous yeast *Rhodosporidium toruloides* is commonly used to produce lipids and their derivatives, including galactitol which can be used to produce polymers with applications in

medicine and as a precursor for anti-cancer drugs [327]. A rare case is described that a halotolerant yeast strain R28 was isolated from mashed soy sauce and identified as *Candida famata* and converts D-psychose to D-talitol (**184**) at a faster rate. In addition, to obtain D-talitol by a fermentation reaction with *C. famata* R28, the conversion coefficient was about 80% at a substrate concentration of 10%, and more than 98% of the consumed substrate was converted to D-talitol [328].

Liamocins are polyol lipids produced by the fungus *Aureobasidium pullulans* and have selective antibacterial activity against *Streptococcus species*. Liamocins produced by *A. pullulans* strain NRRL 50380 on sucrose medium have a D-mannitol head group ester-linked to 3,5-dihydroxydecanoate acyl chains, three or four of which are joined together by 1,5-polyester bonds (liamocins Man-A1 and Man-B1, **193** and **194**, structures are shown in Figure 31), and similar 3′-O-acetylated analogs (Man-A2 and Man-B2, **195** and **196**). Although other types of liamocins are produced depending on the choice of strain and growing conditions. When cultured on a variety of polyols rather than sugars, results in significant structural variations including liamocins with D-sorbitol (**197**, **198**, **199** and **200**), D-galactitol (**201**, **202**, **203** and **204**), D- and L-arabitols, D-xylitol, L-head groups of treitol and glycerol. New variants of liamocin also showed selective activity against *Streptococcus* [198, 263, 264, 329-331]. Liamocins possessed antibacterial activity with specificity against Streptococcus species with MICs ranging from 10 to 78 μg/mL for the following: *S. agalactiae, S. infantarius, S. mitis, S. mutans, S. pneumonia, S. salivarius, S. suis* and *S. uberis* [263, 264, 329, 330].

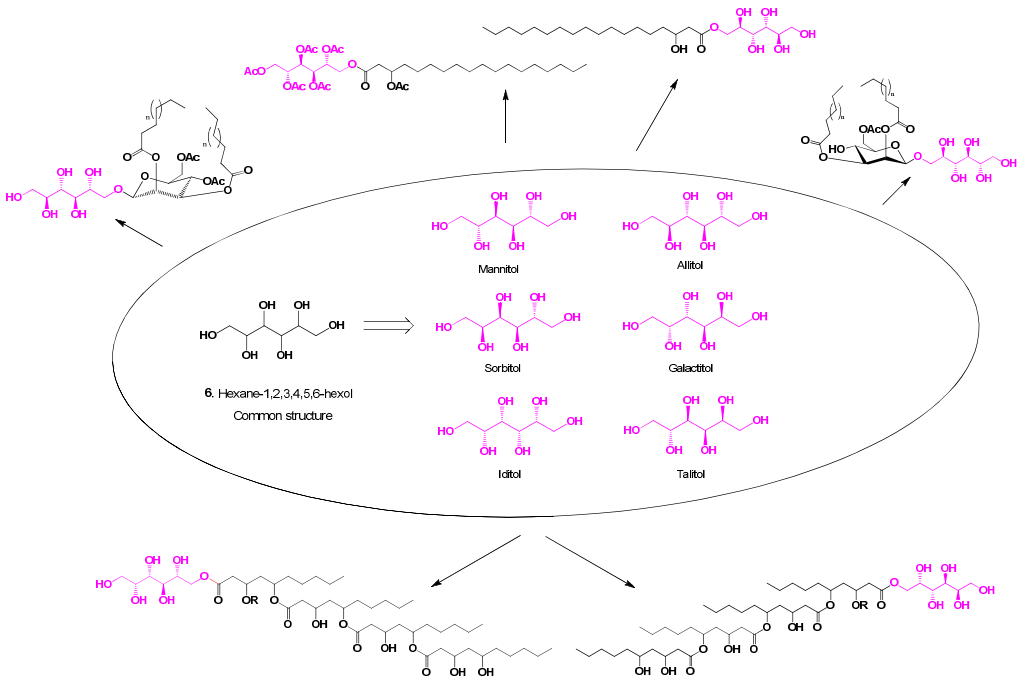

Figure 29. Hexitols, sugar alcohols that include mannitol, allitol, galactitol, sorbitol (D-glucitol), galactiol, iditol, and talitol and contain six hydroxyl groups each found in natural sources.
The most famous of them is mannitol, which is widely distributed in bacteria, yeasts, fungi, algae, lichens, and several plants.

Рис. 29. Гекситы, сахарные спирты, которые включают маннит, аллитол, галактит, сорбит (D-глюцитол), галактиол, идит и талитол.
Содержат шесть гидроксильных групп, каждая из которых содержится в природных источниках. Наиболее известным из них является маннит, широко распространенный в бактериях, дрожжах, грибах, водорослях, лишайниках и некоторых растениях.

Alditol (**180**) was found and isolated from extracts of red algae (class Rhodophyceae): *Bostrychia scorpioide, Chantransia* sp., *Compsopogon hookeri, Halosaccion glandiforme, Rhodella violacea, Polysiphonia lanosa*; brown algae (class Phaeophyceae): *Alaria margiata*, *Asperococcus bullosata, Cymathere desmarestia viridis, Fucus muscoides, Pelvetia canaliculata*, golden algae (class Chrysophyceae), *Ochromonas danica, O. malhamensis, O. minuta, O. sociabilis*, yellow-green algae (class Xanthophymaophyceae): *Heterococcus* sp., *Fragillaria crotonensis, Melosira islandica, Nitzschia palea, Navicula pelliculosa*, cyanobacteria (class Cyanophyceae), *Anabaena cylindrica, Anacystis nidulans, Aphanizomenon flos-aquae, Gloeotriehia echinulata, Nostoc commune*, and a class of predominantly unicellular, flagellated algae (class Prymnesiophyceae): *Coccolithus* sp., *Isochrysis* sp., and *Pavlova lutheri* [331].

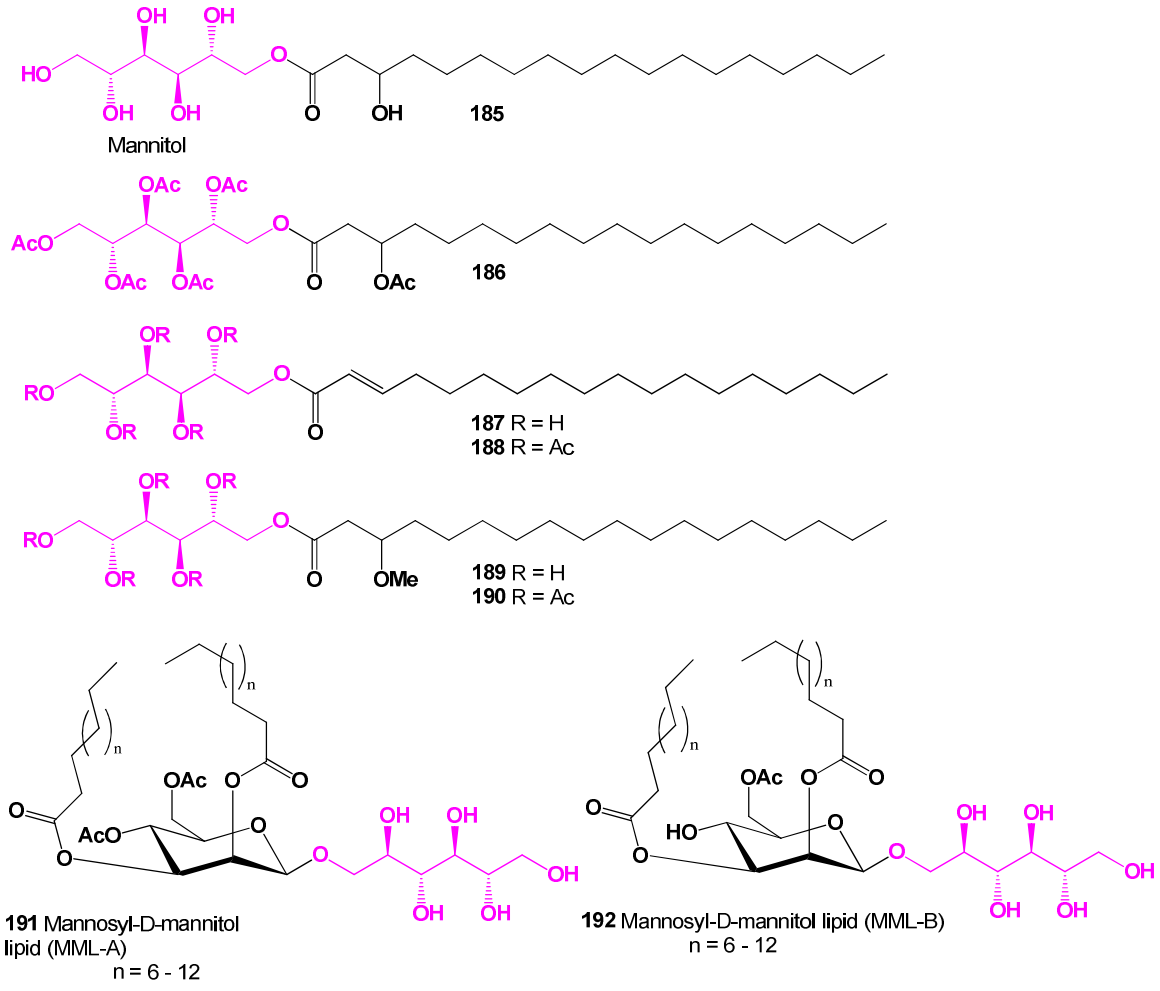

Figure 30. Mannitol fatty acid esters derived from the yeast *Rhodotorula* species.

Рис. 30. Сложные эфиры жирных кислот маннита, полученные из дрожжей вида Rhodotorula.

Liamocins are polyol lipids produced by the fungus *Aureobasidium pullulans* and have selective antibacterial activity against *Streptococcus species*. Liamocins produced by *A. pullulans* strain NRRL 50380 on sucrose medium have a D-mannitol head group ester-linked to 3,5-dihydroxydecanoate acyl chains, three or four of which are joined together by 1,5-polyester bonds (liamocins Man-A1 and Man-B1, **193** and **194**, structures are shown in Figure 31), and similar 3′-O-acetylated analogs (Man-A2 and Man-B2, **195** and **196**). Although other types of liamocins are produced depending on the choice of strain and grow-

ing conditions. When cultured on a variety of polyols rather than sugars, results in significant structural variations including liamocins with D-sorbitol (**197**, **198**, **199** and **200**), D-galactitol (**201**, **202**, **203** and **204**), D- and L-arabitols, D-xylitol, L-head groups of treitol and glycerol. New variants of liamocin also showed selective activity against *Streptococcus* [198, 263, 264, 329-331]. Liamocins possessed antibacterial activity with specificity against Streptococcus species with MICs ranging from 10 to 78 μg/mL for the following: *S. agalactiae, S. infantarius, S. mitis, S. mutans, S. pneumonia, S. salivarius, S. suis* and *S. uberis* [263, 264, 329, 330].

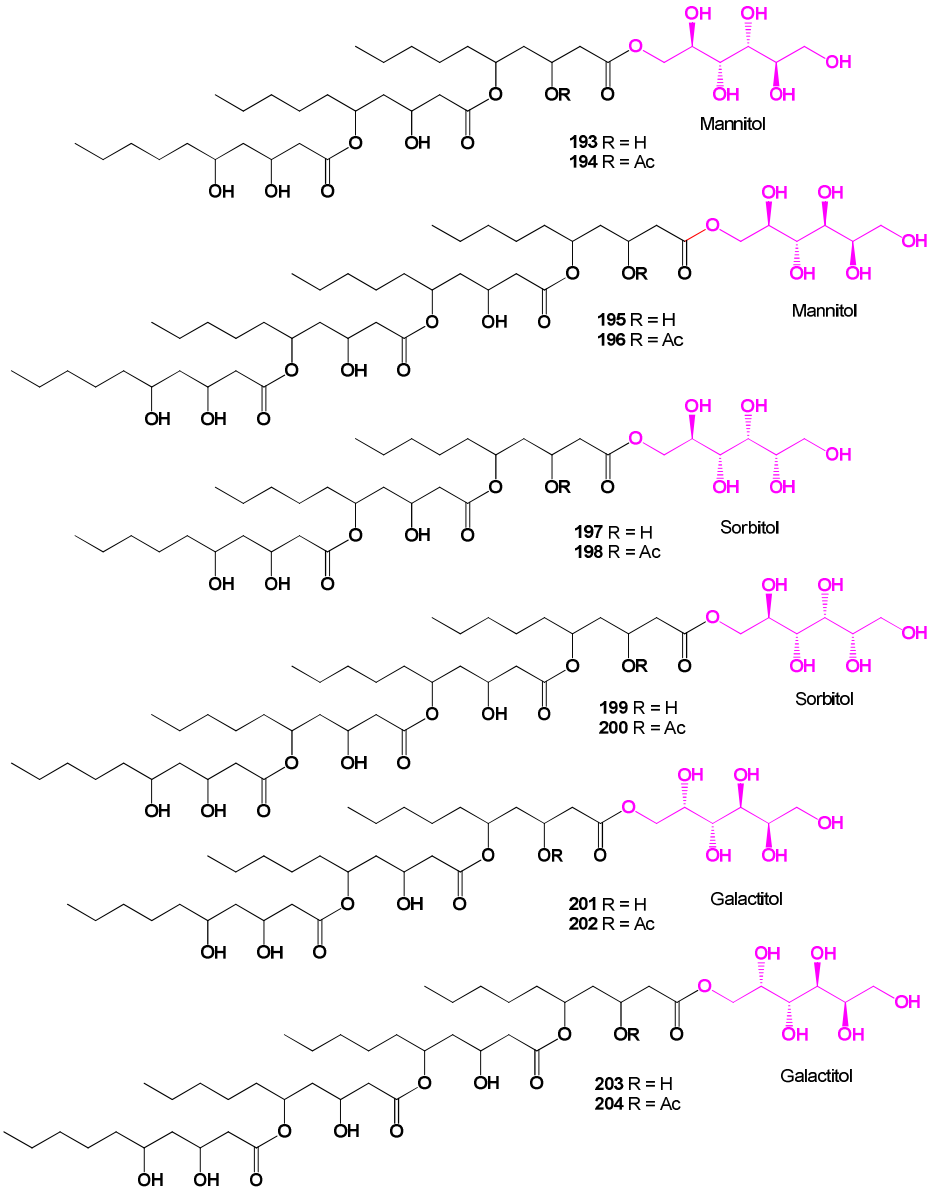

Figure 31. Hexane-1,2,3,4,5,6-hexols derived from the fungus *Aureobasidium*.

Рис. 31. Гексан-1,2,3,4,5,6-гексолы, полученные из гриба *Aureobasidium*.

Alditol (**180**) was found and isolated from extracts of red algae (class Rhodophyceae): *Bostrychia scorpioide, Chantransia* sp., *Compsopogon hookeri, Halosaccion glandiforme, Rhodella violacea, Polysiphonia lanosa*; brown algae (class Phaeophyceae): *Alaria margiata, Asperococcus bullosata, Cymathere desmarestia viridis, Fucus muscoides, Pelvetia canaliculata*,

golden algae (class Chrysophyceae), *Ochromonas danica, O. malhamensis, O. minuta, O. sociabilis*, yellow-green algae (class Xanthophymaophyceae): *Heterococcus* sp., *Fragillaria crotonensis, Melosira islandica, Nitzschia palea, Navicula pelliculosa*, cyanobacteria (class Cyanophyceae), *Anabaena cylindrica, Anacystis nidulans, Aphanizomenon flos-aquae, Gloeotriehia echinulata, Nostoc commune*, and a class of predominantly unicellular, flagellated algae (class Prymnesiophyceae): *Coccolithus* sp., *Isochrysis* sp., and *Pavlova lutheri* [331].

11. Heptane-1,2,3,4,5,6,7-heptaols and octan-1,2,3,4,5,6,7,8-octaols

Very rare complex lipids based on heptane-1,2,3,4,5,6,7-heptaols and octan-1,2,3,4,5,6,7,8-octaols have been found in living organisms, but no data that these lipids are an integral part of biological membranes. And the mathematical model showed that their content in proto membranes should not be less than one percent.

Polyhydric alcohols containing seven hydroxyl groups (seven-carbon sugars) are very rare in nature [332]. Nevertheless, some of them were still found in nature. Only three alcohols containing seven hydroxyl groups such as perseitol (**205**, structures are shown in **Fig. 32**), volemitol (**206**) and β-sedoheptitol (**207**) are known and found in various sources [333].

According to the available information in the literature, volemitol was first discovered in 1895 by the French chemist Émile Bourquelot from the University of Paris in the mushroom *Lactarius volemus*, in addition, D-mannitol was isolated, which was present in the extracts of many studied mushrooms [334]. More than 65 years ago, Lindberg discovered volemitol in lichens of *Rocella lonica*, and in the genus *Dermatocarpon* (family Verrucariaceae) [335-337]. Other researchers also found volemitol and other polyols such as ribitol, arabinitol and mannitol [338, 339].

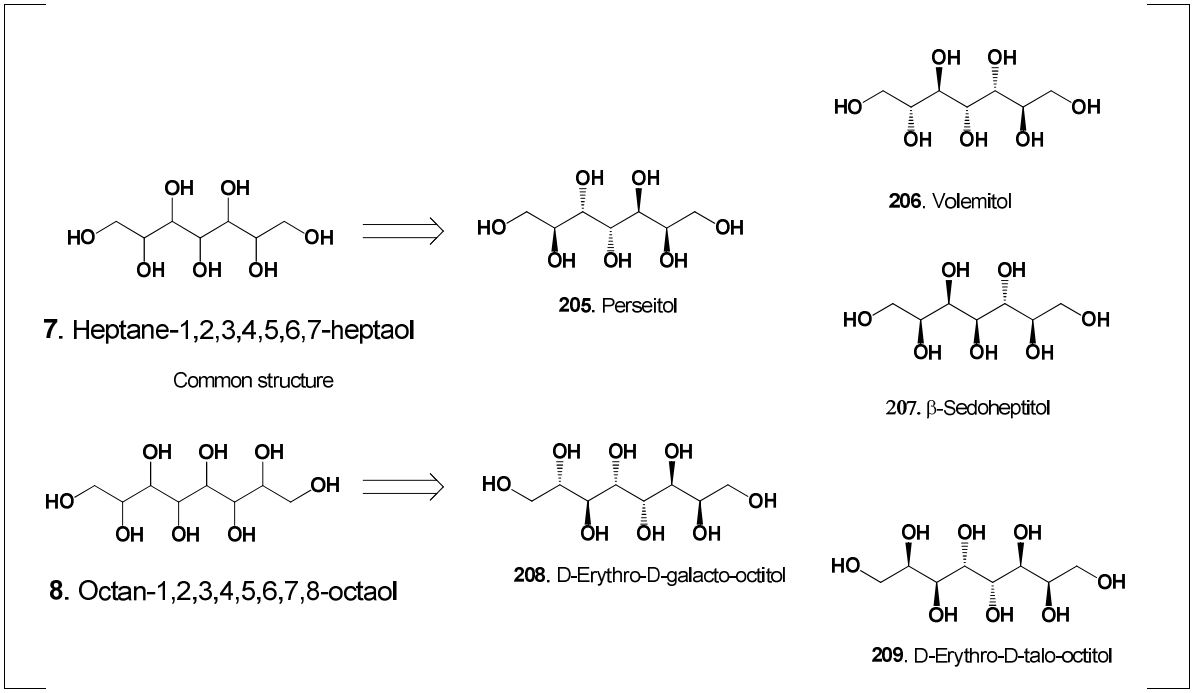

Figure 32. 7 and 8-carbon sugar alcohols derived from plants, fungi, and algae.

Рис. 32. 7- и 8-углеродные сахарные спирты, полученные из растений, грибов и водорослей.

Volemitol (D-glycero-D-manno-heptitol, α-sedoheptitol) is an unusual seven-carbon sugar alcohol. It performs several important physiological functions in some species of the genus *Primula* and is found in the leaves of *Primula polyantha* [340, 341]. Volemitol was isolated from the brown algae *Pelvetia canaliculate*, *Himanthalia elongate, Pelvetia compresssa* and *Hesperophycus californicus* [335, 342-347].

Perseitol (D-glycero-D-galacto-heptitol) was first isolated from the fruits of the avocado (*Persea americana*) Avequin in 1831, 100 years later, E. Le Roy and co-workers in 1931 isolated from the avocado seeds, and Nelson K. Richtmyer in 1970 [348, 349] confirmed the release of this alcohol [350]. Volemitol and β-sedoheptitol were isolated from *Primula officinalis* (family, Primulaceae) [341,351], in addition, perseitol and volemitol were found in extracts of *Hylotelephium spectabile* (formerly called *Sedum spectabile*) [348, 349]. Volemitol was detected in the brown algae *Himanthalia elongate*, *Pelvetia canaliculata*, *Lessonia vadosa*, green alga *Klebsormidium* sp., and in the green alga *Acetabularia* spp. [346, 352-355].

More than 60 years ago, A.J. Charlson and N.K. Richtmyer [356] first discovered, isolated from avocado, and established the structures of D-erythro-D-galacto-octitol (**208**, structures are shown in **Fig. 26**) and D-erythro-D-talo-octitol (**209**), both polyhydric alcohols containing eight hydroxyl groups and are called eight-carbon sugars (called also octitols).

12. Conclusion

Summarizing the data presented in the article, we can conclude that natural low molecular weight polyols form the basis of all complex lipids, regardless of whether they are part of biological membranes or not. In a philosophical model, we have shown that polyols are a trigger for the formation of complex lipids, and, de facto, stimulate the formation of a bilayer lipid protomembrane. The chemical model showed us that protomembranes can contain low molecular weight polyols, which are synthesized spontaneously, depending on the reaction medium, and the mathematical model showed us in what proportion polyols are distributed in protomembranes. The models used showed that in the theoretical distribution of polyols, diols accounted for 40%, which indicates that lipids based on ethylene glycol predominated in the first proto membranes, while glycerolipids accounted for only 33%. Protomembranes consisting of fatty acids and their derivatives can be attributed to a simple type of membrane, however, with the advent of polyols and, accordingly, complex lipids, a new type of protomembrane appears, which was evolutionarily more promising, and subsequently fixed at the genetic level. During evolution, diol lipids were replaced by glycerolipids, which have more suitable physicochemical characteristics for the formation of biological membranes. Other polyols with many hydroxyl groups should have been present in the protomembranes as well, however, over a long historical period, specialization of membranes has occurred, and at present the ratio of polyols is significantly different. Thus, for the first time, using a mathematical model, it was possible to establish what the possible composition of polyols and lipids based on their protomembrane was and how it changed during evolution. Undoubtedly, hydrophobic fragments of complex lipids significantly affect the physical and chemical properties of membranes. Studying these interesting complex lipid synthesis processes using new mathematical models ahead, this article is a prologue to new discoveries.

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МОДЕЛИРОВАНИЕ АБИОТИЧЕСКОГО СИНТЕЗА САХАРНЫХ СПИРТОВ (ГЛИКОЛЯ, ГЛИЦЕРИНА И ДРУГИХ ПОЛИОЛОВ) КАК СТРУКТУРНЫХ ЕДИНИЦ БИОЛОГИЧЕСКИХ МЕМБРАН

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Аннотация. Предположение о том, что морская вода является колыбелью происхождения примитивных живых организмов, не вызывает сомнений. Никто не знает, как это произошло, но предположений много, хотя доказательная база всех этих предположений вызывает много вопросов. Эта статья представляет собой попытку выяснить происхождение протомембраны и ее превращение в двухслойную липидную мембрану в неживом веществе. Предположительно, протомембраны, состоящие из жирных кислот и других амфифилов, были простым типом мембран, но с появлением полиолов и, соответственно, сложных липидов появляется новый тип протомембран. Возможно, этот новый тип протомембраны, состоящей из сложных липидов, стал началом возникновения будущей биологической мембраны и всего живого на Земле. Коацерваты из гипотезы Опарина – Холдейна использовались в качестве модели для объяснения образования протомембран. Химическая модель показывает, какие полиолы могли спонтанно образовываться в первичном бульоне, а математическая модель показывает, что на этиленгликоль (40%), глицерин (33%), бутан-1,2,3,4-тетраолы (17%) приходится 90% всех производимых полиолов. Это указывает на возможное преобладание диольных липидов в первичных примитивных протомембранах. В ходе химической эволюции и при изменении температуры, pH и условий окружающей среды диольные липиды замещались глицеролипидами, обладающими более подходящими физико-химическими характеристиками для формирования биологических мембран всех живых организмов. В статье представлены полиолы в составе сложных липидов, встречающихся в современных биологических мембранах.

Ключевые слова: эволюция, коацерваты, гипотеза Опарина – Холдейна, липиды, протомембраны, полиолы.