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PHOTOCHEMISTRY

Formation of Chiral Structures in Photoinitiated Formose Reaction

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Abstract—The possibility to synthesize biologically important sugars and other chiral compounds without any initiators in the UV-initiated reaction of formaldehyde in aqueous solution has been shown for the first time. An optically active condensed phase due to an sp^3-hybridized carbon atom has been detected. It has been shown that this phase is formed due to the spatial cleavage of antipodes in the racemate, similar to the cleavage of enantiomers following the sign of chirality in the known experiments of Pasteur. The results have been obtained under the conditions that correspond to modern ideas about the form and vector of prebiological evolution and, therefore, can be of fundamental importance for understanding the processes of biopoiesis.

Keywords: biopoiesis, chirality, formose reaction, formaldehyde, photoionization

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INTRODUCTION

Compounds with optically active (chiral) carbon atoms provide the basis for biopoiesis—the process of transformation of the inanimate nature into the living nature. This is one of the most significant cross-cutting trends in chemical and biological evolution [1]. In particular, the polypeptide chain of proteins consists of residues of L-amino acids, whereas D-deoxyribose forms polymer chains of the double helix of DNA. Except for special cases, carbohydrates and lipids are also homochiral. The basis for chirality of molecular structures in living systems is carbon in sp^3 hybridization.

Asymmetric carbon could enter the organic world at the stage of the primary atmosphere of the planetesimal, containing formaldehyde $H_2C{=}O$ (FA) [2], for example, through the Butlerov autocatalytic reaction (the formose reaction[1] in foreign terminology) (see reviews [3–6]), in which any monosaccharides or other organic compounds capable of producing enediol forms can act as an autocatalyst ("seed") [7, 8]. In these chemical reactions, a set of monosaccharides was found, starting with the simplest C_2 glycolic aldehyde, up to C_8. On the other hand, it is possible to initiate the conversion of formaldehyde into sugars by physical action: radiolysis [9] or UV irradiation [10–14]. The factor common for these works is the mandatory use of the main catalysts ($CaCO_3$, $Ca(OH)_2$, Na_2CO_3, $NaHCO_3$, NaOH, $Mg(OH)_2$ (except for [14]), as well as the use of dilute aqueous solutions. From the point of view of physicochemical modeling of the synthesis of macromolecules from maximally simple precursors (de-novo), it is, of course, preferable to carry out the formose reaction under the action of UV in gas (vapor) or equally concentrated water phase containing only FA molecules.

It is well known that the absorption band of the carbonyl group of the FA molecule has a maximum at 260 nm with an absorption coefficient $\varepsilon < 100$ L/(mol cm) [14]. However, in aqueous solution, FA interacts with water molecules to form methylene glycol (MG), which absorbs radiation with a shorter wavelength, whose concentration in dilute solutions is much higher than the concentration of free FA molecules. Therefore, absorption of a quantum of light with a wavelength $\lambda \le 260$ nm by FA molecules leads to breaking the O–H and C=O bonds in the MG and FA molecules, respectively, to form reactive species. It is reasonable to assume simultaneous occurrence of at least two groups of parallel reactions:

[1] Formose is a mixture of synthetic carbohydrates—sugars obtained from FA in the Butlerov reaction.

(1) polymerization of MG ($CH_2(OH)_2$) to form paraformaldehyde (PF) $n(HO–CH_2–OH) \rightarrow (H_2CO)_n + nH_2O$;

(2) oligomerization of FA to form mono-, di-, and polysaccharides:

$$H–CH=O + H–CH=O \rightarrow CH_2OH–CH=O +$$
$$H_2C=O \rightarrow CH_2OH–CHOH–CH=O + \text{... etc.}$$

The above background served as the basis for performing this work, whose aims were as follows:

—to study the possibility of the formation of chiral products (sugars and others) upon UV photolysis with a wavelength of $\lambda = 254$ nm of an aqueous FA solution in the absence of any catalysts;

—to study the possibility of formation of macroscopic chiral phases in the products of this reaction.

This work models the processes which, in the framework of modern concepts, could actually take place at the stage of the primary atmosphere of the planetesimal. It is quite obvious that carrying out such physicochemical modeling is of interest for understanding the processes of biopoiesis.

EXPERIMENTAL

We used in the experiments a highly concentrated (95%) solution of FA in water, obtained by decomposition of paraformaldehyde at 160–170°C for 1.5 h. The mass of the initial solution was 600 g. UV irradiation was carried out with a DRSh-100 lamp (without a filter) onto the exposed surface of the solution placed in a glass 2-L beaker, with continuous stirring. The distance between the lamp and the surface of the solution was 10 cm. To eliminate the spontaneous low-temperature conversion of FA to PF, a thermostating temperature of 70°C was chosen. The experiment was terminated in 8.5 h after complete solidification of the initial solution.

The main (by mass) product formed was paraformaldehyde. This reaction, side for us, occurs according to scheme (1) (see above). Due to the expected small yield of the sugars formed according to scheme (2) and in order to minimize the losses upon separation of the desired carbohydrates from PF, sublimation of PF obtained upon irradiation, enhanced by evacuation, was chosen. The residual vapor pressure of PF permitted us to do this under rather mild conditions (70–80°C), but for a long time (265 h). The total yield of nonvolatile products was no less than 0.7 wt %. This product will be further referred to as analyte-1. A qualitative analysis of analyte-1 for sugars was carried out using the classical Fehling reagent as follows: potassium tartrate (150 g) was dissolved in a 1-L flask in 600–700 mL of sodium hydroxide solution with a density of 1.12. To the resulting potassium–sodium tartrate, a solution of copper sulfate (34.636 g $CuSO_4$ per 160 mL water) was gradually added. The resulting clear solution was diluted with water to 1 L. The Fehling reagent (1 mL) and water (1 mL) with 30 mg of our product were poured into a test tube. The upper part of the test tube was heated until the beginning of boiling. The top layer turned first yellow (Cu(OH)) and then red-orange (Cu_2O).

To determine the composition of the organic products of the reaction, gas-liquid chromatographic-mass-spectrometric (GLC-MS) analysis was used with preliminary derivatization by the silylation method [15]. The initial sample (analyte-1) was separated by dissolving in water under room conditions into the water-soluble fraction (with subsequent evaporation) (analyte-2) and the water-insoluble fraction (precipitated for 24 h; then the amount of the precipitated substance remained unchanged) (analyte-3).

The samples of analyte-2 and analyte-3 for GLC–MS analysis were prepared by two methods.

The first method: 20 mg of each sample was dissolved in 2 mL of distilled water.

The second method: hydrolysis of the samples obtained upon irradiation (oligomeric compounds) was carried out in order to obtain monomeric molecules. For this purpose, 20 mg of each sample was placed in 150 mL of a 1 mol/L HCl solution and heated in a boiling water bath for 2 h with constant agitation with a magnetic stirrer. To prevent evaporation of water and other components of the reaction mixture, reflux condensers were used.

The analysis of samples of analyte-2 and analyte-3 and their hydrolysates for the content of monosaccharides and other organic compounds was carried out by the of GLC-MS method with preliminary derivatization by the silylation method [8].

Chromatographic–mass spectrometric analysis of the derivatized samples was carried out on an Agilent 7000B instrument (USA) equipped with an Hp-5ms capillary column measuring 30 m × 0.25 mm × 0.25 μm. The chromatographic conditions were as follows: gradient heating of the column from 80 to 280°C at a speed of 8°C/min.

The phase transition temperatures were determined using a differential chromel–alumel thermocouple, an F116/2 microampere meter, and a U800X digital microscope.

Thin layer chromatography was also used for the studies.

The optical activity of aqueous solutions (dispersions) of analyte-1, analyte-2, and analyte-3 was studied using a polarimeter with a cell 20 cm long.

Optical microscopy in transmitted light (using a MIKMED-6 microscope) of xerogel (or dispersed precipitate) of analyte-1 obtained by slow drying of its aqueous solutions (dispersions) on a slide was carried out. A polarizer was placed between the light source and the slide, and an analyzer (that is, the second polarizer) between the slide and the microscope

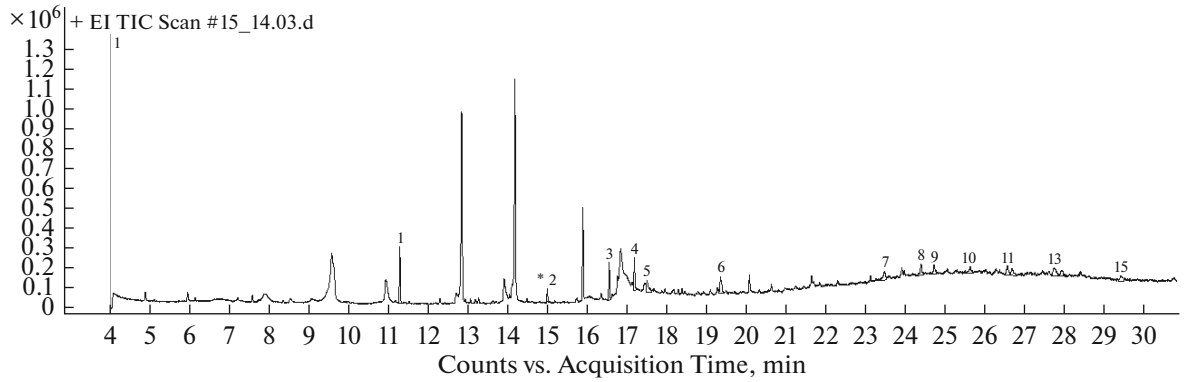

Fig. 1. Chromatogram of the analyte-2 sample derivatized by silylation.

objective. The polarizer and analyzer axes were directed at an angle of 90° (dark field regime).

RESULTS AND DISCUSSION

The product (analyte-1) obtained by irradiation of the initial FA solution with UV light has a brownish color. The product is practically insoluble in hexane, ethyl acetate, acetone, glycerol, ammonia, hydrogen peroxide, and slightly soluble in water. It is readily soluble in benzene, cyclohexane, chloroform, carbon tetrachloride. Solutions or dispersions of analyte-1 are optically inactive. The water-soluble portion of the product is also optically inactive (analyte-2). It is a white compound, viscous at room temperature; its boiling point is 118°C at 760 mm Hg. The water-insoluble fraction (analyte-3) is a beige-colored crystalline compound; its melting point is 137.5°C; its aqueous dispersion is also optically inactive. The absence of optical activity of the solutions or dispersions is quite an expected result, since there is no significant chiral asymmetric factor in the reaction under study, and the reaction products are racemic.

Qualitative analysis of analyte-1 for monosaccharides was carried out using the freshly prepared Fehling reagent. The analysis is based on the reducing ability of sugars [16]. It showed the presence of reducing carbohydrates in this product. It is well known that all monosaccharides and only a part of disaccharides (lactose, maltose, and cellobiose) belong to such carbohydrates. Therefore, it is reasonable to assume the presence of some of these biologically important sugars containing an asymmetric carbon atom in analyte-1.

An evaluation of the type of sugars in analyte-1 was also carried out by thin layer chromatography using a SiO_2 sorbent and an eluent consisting of a mixture of cyclohexane–benzene–methanol taken in a volume ratio of 2 : 3 : 1. Comparing the retention factors R_f obtained for chromatograms of analyte-1 (0.935) and for a number of trial sugars (rhamnose with the number of C atoms of 6 (0.944), glucose-C_6 (0.947), arabinose-C_5 (0.976), xylose-C_6 (0.977), and sucrose-C_{12} (0.923)), it can be seen that the sugars tested, contained in analyte-1, can belong to the group of sugars with the number of carbon atoms within 12, which does not contradict the data obtained in the Fehling reaction.

The qualitative composition of products obtained upon photolysis was more precisely determined by the GLC-MS method. The results of analysis of the analyte-2 and analyte-3 samples prepared by the first method, that is, dissolved in distilled water and derivatized, are shown in Figs. 1, 2 and Tables 1, 2, respectively. The tables show decoding of chromatographic peaks, including the retention times and peak areas, as well as the percentage of individual peaks with respect to the total area of all peaks.

Analyte-2 sample (Fig. 1, Table 1). According to the results of the GLC-MS analysis, 3 peaks of 16 were identified, which comprised 32% of the total area of all peaks. Note that here and below, the notation D(L) is introduced to emphasize that GLC-MS does not distinguish antipodes. It was shown that about 13.8% was glycerol, followed by D(L)-xylopyranose (9.1%) and β-D(L)-(+)-xylopyranose (9.1%).

Analyte-3 sample (Fig. 2, Table 2). 8 peaks of 22 were identified, which comprised 63% of the total area of all peaks. Polyol glycerol and polyol of undetermined structure (peak 3) comprised 12.6%, glycolic acid 11.8%, and glycolic aldehyde 4.5%. The relative content of monosaccharides was close to 34%: two of them were not identified (peaks 7 and 12), fructose comprised 13.9%, and galactose ~2%.

The results of the GLC-MS analysis of the derivatized hydrolyzate of the analyte-2 sample are shown in Fig. 3, and the decoding of the most probable compounds corresponding to the chromatographic peaks is shown in Table 3. It should be noted that 16 of 17 peaks are identified. According to the data obtained, the predominant products are polyols: diols (peaks 1, 3, 5–8), glycerol (peak 4), ribitol (peak 12),

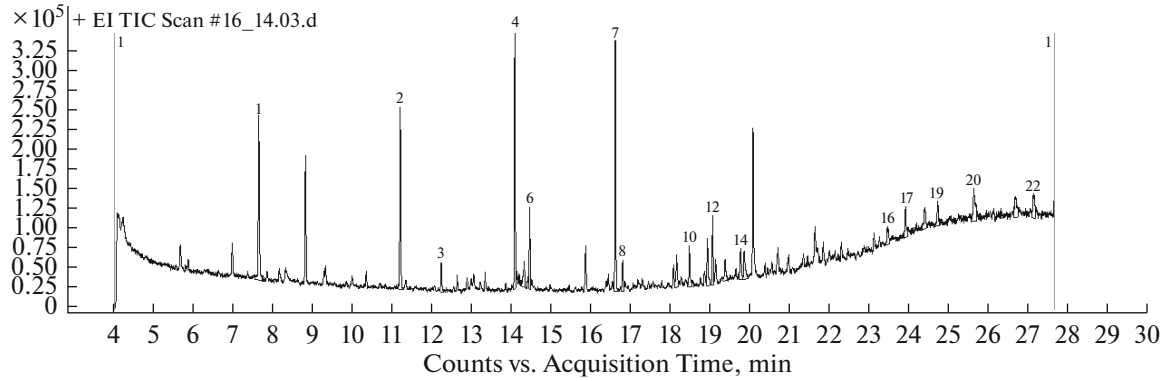

Fig. 2. Chromatogram of the analyte-3 sample derivatized by silylation.

unidentified polyol (peak 13), and erythritol (peak 14). The total content of polyols was 76.1%, of which the highest content (37.2%) corresponds to glycerol, then 2-butene-1,4-diol (13.1%), 3-methylene-1,4-diol-butane (10.3%), and others. The following sugars were detected: fructose (12.4%), xylose (0.9%), and disaccharide sucrose (1.1%).

The results of the GLC-MS analysis of the derivatized hydrolyzate of the analyte-3 sample are shown in Fig. 4, and the decoding of the most probable compounds corresponding to the chromatographic peaks is shown in Table 4. The structure of 18 peaks out of 31 was established, which comprised 49% of the total area of the peaks. Five different polyols were found, with the content of glycerol (33.8%) being the highest, and lower contents of ethylene glycol (0.73%), 2-butene-1,4-diol (0.57%), erythritol (1.12%), and ribitol (0.5%). The total percentage of branched deoxysaccharides (D(L)-erythro-pentitol-2-deoxy, D(L)-pentofuranose-2-deoxy, and D(L)-arabinohexitol-2-deoxy) was 3.3%. The contents of lactic acid (peak 2) and lactaldehyde (peak 16) were close to 1.3 and 1.1%, respectively. Disaccharides trehalose and maltose (1.5% in total), monosaccharides lyscopyranose (1.7%), talopyranose (0.17%), glycopyranose (0.9%), fructose (0.64%), and a sugar of undetermined structure (peak 23, 0.72%) were identified.

Hence, the analyte-2 and analyte-3 samples contained significant amounts of polyols of different structures, monosaccharides, and disaccharides; and deoxy sugars are found in the analyte-2 sample. Hydrolysis of both samples permitted us to specify the

Table 1. Components of the analyte-2 sample, specifying the numbering of peaks, retention times, peak areas, and their percentage with respect to the total area of peaks

Peak number	Retention time	Area	Area, %	Compound
1	11.292	455251	13.82	Glycerol
2	15	81010	2.46	
3	16.559	299785	9.1	(L,D)-Xylopyranose
4	17.192	300088	9.11	β-(L,D)-(+)-Xylopyranose
5	17.512	238904	7.25	
6	19.357	246149	7.47	
7	23.478	206333	6.26	
8	24.402	166998	5.07	
9	24.728	140863	4.28	
10	25.636	146532	4.45	
11	26.574	166790	5.06	
12	26.681	157450	4.78	
13	27.746	216093	6.56	
14	27.933	162195	4.92	
15	29.421	132042	4.01	
16	36.269	177290	5.38	

Table 2. Components of the analyte-3 sample, specifying the numbering of peaks, retention times, peak areas, and their percentage with respect to the total area of peaks

Peak number	Retention time	Area	Area, %	Compound
1	7.643	440590	11.8	Glycolic acid
2	11.202	401763	10.76	Glycerol
3	12.232	69146	1.85	Polyola
4	14.084	517897	13.87	(L,D)-Fructose
5	14.319	83669	2.24	
6	14.457	167139	4.48	Glycolic aldehyde
7	16.61	527763	14.14	Sugar?[a]
8	16.796	74051	1.98	
9	18.151	96235	2.58	
10	18.475	99470	2.66	
11	18.929	133416	3.57	
12	19.058	144972	3.88	Sugar?[a]
13	19.373	72876	1.95	Galactose?[a]
14	19.765	88557	2.37	
15	19.855	104707	2.8	
16	23.456	67562	1.81	
17	23.91	91200	2.44	
18	24.396	94838	2.54	
19	24.721	77624	2.08	
20	25.63	165912	4.44	
21	26.672	106083	2.84	
22	27.131	108029	2.89	

[a] The most probable of the compounds proposed by the database.

list of monomeric compounds involving in the polymer structures. The optical isomers (enantiomers) of practically all chiral products found in the formose reaction are of considerable functional significance in natural systems (see Table 5) [10].

To study the optical activity of products of FA photolysis, xerogels (dispersed precipitates) of analyte-1, and water-soluble (analyte-2) and water-insoluble (analyte-3) products obtained by slow drying of their aqueous solutions (dispersions) on a slide were used.

Figure 5 shows the results of optical microscopy of xerogel (dispersed precipitate) of analyte-1 in polarized light. It can be clearly seen that a significant portion of the xerogel (or dispersed precipitate) structures

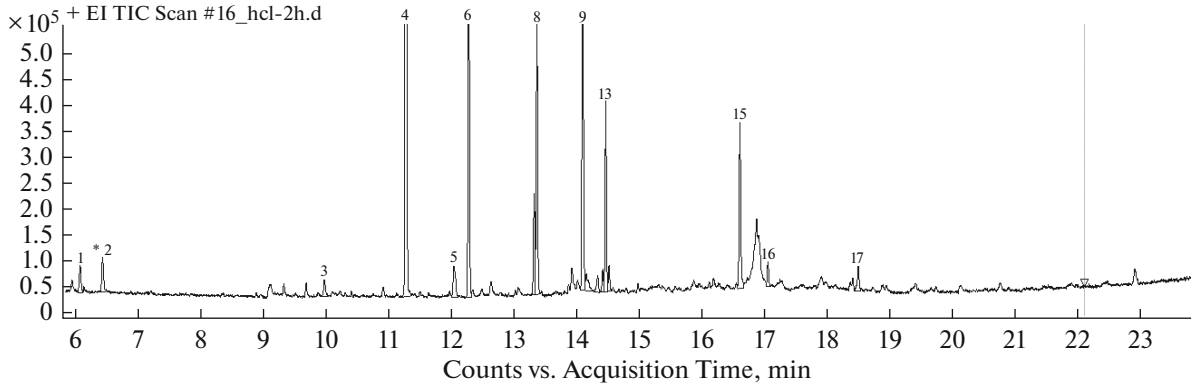

Fig. 3. Chromatogram of the analyte-2 sample derivatized by silylation after acid hydrolysis with 1 M HCl for 2 h.

Table 3. Components of hydrolysate of the analyte-2 sample, specifying the numbering of peaks, retention times, peak areas, and their percentage with respect to the total area of peaks

Peak number	Retention time	Area	Area, %	Compound
1	6.073	103749	1.17	Ethylene glycol
2	6.431	131994	1.49	Ethyl lactate
3	9.971	74874	0.84	diola
4	11.272	3299798	37.22	Glycerol
5	12.039	167528	1.89	diola
6	12.273	1163630	13.13	2-Butene-1,4-diol
7	13.318	297939	3.36	2-Propanone-1.3-diol
8	13.361	912410	10.29	3-Methylene-1,4-diol-butane
9	14.092	1099177	12.4	Fructose
10	14.152	107002	1.21	
11	14.331	66029	0.74	Sugara
12	14.412	65543	0.74	Ribitol
13	14.459	570575	6.44	Polyol?[a]
14	14.511	76797	0.87	Erythritol
15	16.6	553715	6.25	4-Ketoglucose??[a]
16	17.049	79435	0.9	Xylose
17	18.488	94526	1.07	Sucrose

[a] The most probable of the compounds proposed by the database.

obtained, glow on slides when the analyzer is positioned perpendicular to the polarization plane of light passing through the sample, that is, in the dark-field regime (Fig. 5). This means the presence of optical activity in the condensed phase of the xerogel structures of the analyte-1 sample. The portion of optically inactive structures in analyte-1 xerogel, according to a visual estimate (Fig. 5), is negligible.

In the sample as a whole, the antipodes, that is, the left and right isomers of chiral products of photolysis, are formed in the same amounts. This follows from the equal reaction rates of the synthesis of antipodes, which, in turn, follows from the conservation of parity in electromagnetic interactions. Therefore, the only reason for the formation of the optically active structures detected can be the spatial cleavage of the antipodes in the racemate, similar to the cleavage of enantiomers following the sign of chirality in the known experiments of Pasteur [18].

Since in this case, this is a fairly realistic model of processes in the primary atmosphere of the Earth, this experiment demonstrates that spontaneous formation of chiral compounds (sugars) and subsequent spontaneous spatial separation of antipodes to form macroscopic fragments of chiral (optically active) phases in systems similar to prebiological systems, can occur

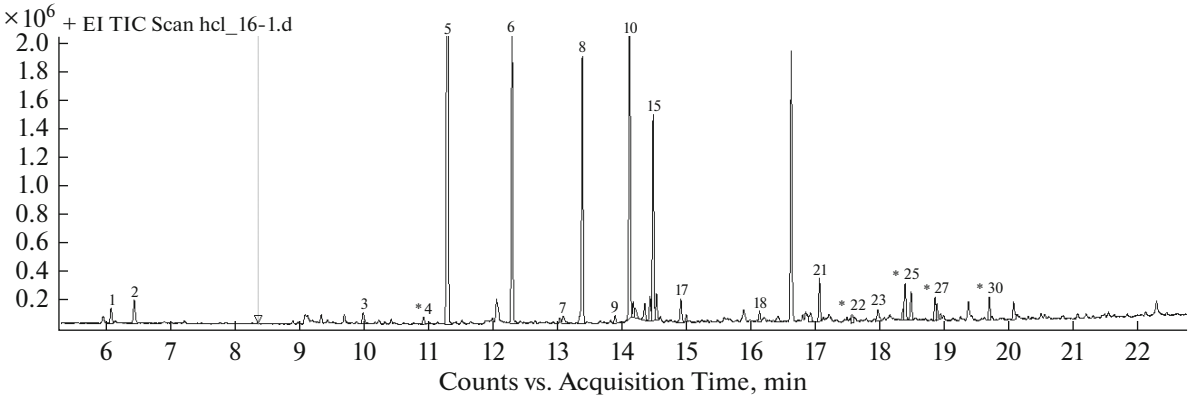

Fig. 4. Chromatogram of the analyte-3 sample derivatized by silylation after acid hydrolysis with 1 M HCl for 2 h.

Table 4. Components of hydrolysate of the analyte-3 sample, specifying the numbering of peaks, retention times, peak areas, and their percentage with respect to the total area of peaks

Peak number	Retention time	Area	Area, %	Compound
1	6.078	204113	0.73	Ethylene glycol
2	6.437	348061	1.25	Lactic acid
3	9.984	200382	0.72	
4	10.923	87073	0.31	
5	11.291	9395519	33.78	Glycerol
6	12.291	3455734	12.42	
7	13.088	158491	0.57	2-Butene-1,4-diol
8	13.381	3050557	10.97	
9	13.888	97263	0.35	
10	14.113	3974000	14.29	(L, D)-Fructose
11	14.172	176658	0.64	
12	14.203	152499	0.55	
13	14.349	222474	0.8	
14	14.432	251139	0.9	
15	14.48	2295983	8.25	
16	14.532	293513	1.06	Lactic aldehyde
17	14.909	311569	1.12	Erythritol
18	16.13	121680	0.44	
19	16.416	113041	0.41	
20	16.919	168934	0.61	
21	17.057	478846	1.72	Lyxopyranose
22	17.563	140672	0.51	Ribitol
23	17.965	200599	0.72	Sugar?[a]
24	18.361	126112	0.45	(L, D)-Erithro-pentitol-2-deoxy?[a]
25	18.384	450204	1.62	(L, D)-Erithro-pentofuranose-2-deoxy?[a]
26	18.478	335549	1.21	(L, D)-Arabino-hexitol-2-deoxy?[a]
27	18.847	274633	0.99	Beta-(L, D)-Methylfructofuranoside?[a]
28	18.878	162409	0.58	Trehalose
29	18.936	48612	0.17	β-(L, D)-(+)-Talopyranose
30	19.692	270387	0.97	Maltose?[a]
31	20.066	247706	0.89	Glucopyranose?[a]

[a] The most probable of the compounds proposed by the database.

even in solutions of compounds with molecular masses of no more than $\mu \sim 10^2$ Da, that is, much earlier than the chiral macromolecules were formed.

CONCLUSIONS

In summary, in the physicochemical modeling of de-novo, by photolysis of a concentrated solution of formaldehyde and subsequent condensation of the product of the formose reaction, the following experimental results have been obtained:

(1) The possibility of synthesizing biologically significant sugars and other chiral compounds without any initiators in the UV-initiated reaction of formaldehyde in an aqueous solution has been shown for the first time.

(2) An optically active condensed phase due to sp^3-hybridized carbon atom has been detected.

(3) It has been shown that the optically active condensed phase is formed due to the spatial cleavage of the antipodes in the racemate, similar to the cleavage of enantiomers following the sign of chirality in the known experiments of Pasteur.

Table 5. Biological significance of the compounds obtained in the reaction

No.	Compound	Functional significance
1	Glycerol	The basic molecule from which triglycerides are formed, which are important components in the process of metabolism in living organisms
2	Xylose	Participates in the processes of mutual transformations of carbohydrates, contained in plant embryos as an ergastic compound
3	Fructose	Contained in honey and some fruits, used to produce energy in the liver during glycolysis; as a monosaccharide unit, included in sucrose and lactulose
4	Sucrose	Natural carbohydrate used for food, the main constituent of cane sugar and sugar beet
5	Glycolic acid	Included in the group of fruit alpha-hydroxy acids
6	Glycolic aldehyde	Precursor of many biologically active compounds, for example, amino acid glycine; as intermediate, involved in some biochemical processes, for example, in catabolism of purines
7	Galactose	Incorporated in oligosaccharides (melibiose, raffinose, stachyose), some glycosides, plant and bacterial polysaccharides (gums, mucus, galactans, pectins, hemicelluloses); in the body of animals and humans, in lactose, group-specific polysaccharides, cerebrosides, keratosulfate, and others. In animal and plant tissues can be involved in glycolysis, turning into glucose-1-phosphate, which is assimilated
8	Polyhydric alcohols	Contained in mushrooms, fruits, and vegetables, as well as in humans and animals (erythritol); ribitol is incorporated in riboflavin and flavinadenine dinucleotides and is present in the cell walls of gram-positive bacteria
9	Deoxysugars	Components of glycoside, oligo- and polysaccharides; their important representative 2-deoxy-D-ribose is in the composition of deoxyribonucleic acids (DNAs)
10	Lactic acid	Produced by the degradation of glucose, forms in muscles
11	Trehalose	Possesses therapeutic properties at the cell level, controlling the unfolding of proteins, in the larvae of the chironomid Polypedilum vanderplanki, capable of withstanding drying, the accumulation in the cells of a large concentration of trehalose is one of the mechanism of resistance to drying
12	Maltose	In animal and plant organisms, maltose is formed during the enzymatic cleavage of starch and glycogen
13	Lyscopyranose	In nature it is extremely rare, for example, as a component of some bacterial glycolipids
14	Glucopyranose	The monomer from which the two most important polysaccharides starch and cellulose are formed

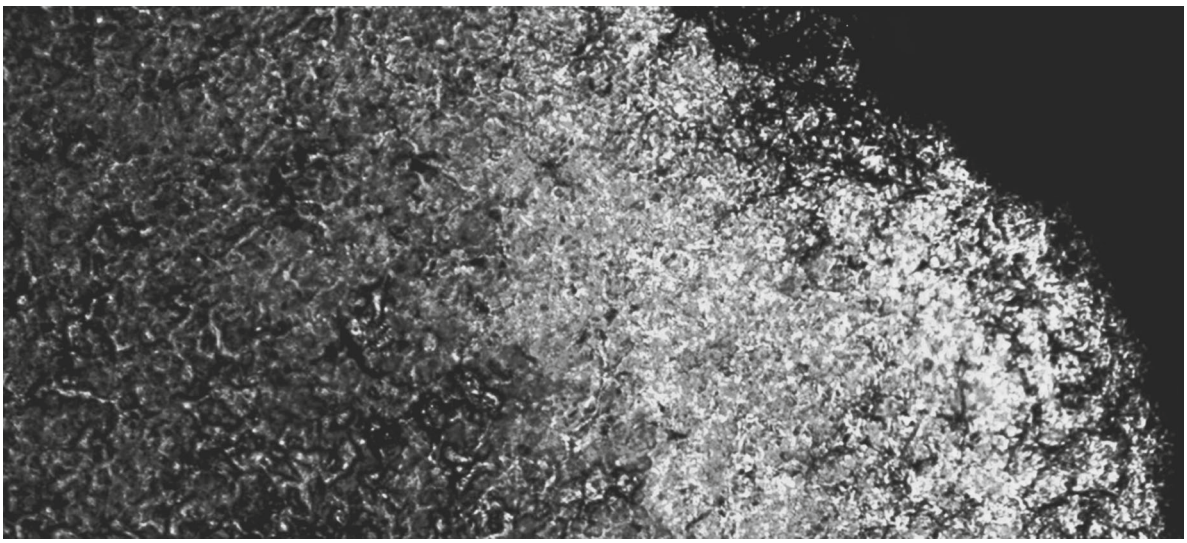

Fig. 5. Microphotograph (magnification ×40) of xerogel (dispersed precipitate) of analyte-1 in a polarizer and analyzer crossed at 90° (dark field regime). The ratio of white–black contrast indicates a much larger proportion of optically active condensed phases in the xerogel, in comparison with optically inactive phases.

These experimental results have been obtained under conditions corresponding to modern concepts of the form and vector of prebiological evolution, and therefore may be of fundamental importance for understanding the processes of biopoiesis.

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