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PRELIMINARY RESULTS OF GLUCOSE OXIDATION BY PHOTOCATALYSIS ON TITANIUM DIOXIDE - PRIMARY INTERMEDIATES

In the presented paper preliminary results of glucose oxidation on illuminated titania are reported. For comparison, results of direct glucose photolysis are also included. At high glucose concentration, up to 1.4 g/dm^3, the yield of 3 hour reaction, determined by COD measurements, was small and amounted to about 5.8%. Additionally, pH measurements show, that oxidation of glucose leads to formation of acidic compounds – after 3 hours the pH lowered from 6.5-6.8, depending on glucose concentration, to about 4.5. Attempt has been undertaken to identify some of the intermediates of the photocatalytic reaction using GC-MS analysis of specially treated samples of the reactor slurry. The analysis showed the existence of intermediates which were formed both as a result of intramolecular changes and of oxidation reactions. Five acidic derivatives were found among the intermediate compounds.

keywords: photocatalysis, TiO₂, glucose, primary intermediates

1. INTRODUCTION

Food industry constitutes one of the most important parts of the world economy. It gives also huge amount of solid and liquid wastes which have to be utilized. The

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wastes, usually not toxic both for humans and animals, have been broadly utilized as animal food or they serve as raw materials in many fields of food and other industries. However, even these not toxic wastes become very harmful for natural environment if their concentration in waters exceeds certain level. Sewage from food industry are highly loaded with various organics possessing reductive character, and raising strongly because of that water COD and BOD indexes. The sewage contain also other pollutants, as for example purifying agents (e.g. detergents), lubricants etc. [1]. The sewage from food industry contain first of all water-soluble carbohydrates, the main ingredient of plants and plant food. On the one hand the mono- and oligosaccharides can serve as food for any microorganisms widely utilized in biological sewage-treatment plants [2]. On the other, these usually highly reductive compounds pose, unfortunately, a serious threat for any aqueous livings, both for water plants and animals.

Until now the sewage from food industry are purified using mainly biological methods. The processes base on special metabolisms of some of bacteria, transforming organics containing in water into mineral compounds. At present the methods of sludge digesters (producing methane) become popular, especially in the case of highly loaded sewage. Also small, home sludge digesters have appeared in some farms [2,3].

Since more than twenty years a research has been undertaken on practical application of Advanced Oxidation Processes for purification of industry sewage, including food industry. AOP`s methods utilise highly reactive $OH^{\bullet}$ radicals generated *in situ* in various ways. Organic matter is usually fully mineralised, i.e. to CO_2 and H_2O [4-7]. The processes such as photocatalysis on semiconductors, H_2O_2 action, ozonation, Fenton and photo-Fenton reactions, electrochemical oxidation, and also their combinations, are good examples of the Advanced Oxidation Processes. Among the AOP's photocatalysis on semiconductors seems to be the most promising. The process needs only a photoactive semiconductor and appropriate light - UV part of solar spectrum is sufficient for excitation of semiconductor electrons. Titanium dioxide serves mainly as the semiconductor: the compound, besides its high photoactivity, is very stable chemically and photochemically, non-toxic and relatively cheap [3,5,8]. Many compounds such as carboxylic acids, organic dyes, phenols, pesticides, surfactants, some of inorganic compounds, and many others are fully mineralized by photocatalysis on TiO_2 [9,10]. One should remember, however, that the photocatalytic processes are efficient only at low concentration of water contaminants. Therefore, they can be regarded as the so called tertiary methods of water purification.

Illumination of a semiconductor with a light of an appropriate energy ($h\upsilon \geq E_g$, E_g – width of a semiconductor forbidden band) causes formation of free electrons (electrons in semiconductor conduction band) and holes in semiconductor valence band. If their lifetime is sufficiently long they can react with some molecules reducing (electrons) or oxidising (holes) them. Full set of initiated by the light reactions has been reported in

literature [11-13]. The excited electrons reduce oxygen molecules dissolved in water. The holes react mainly with water molecules or with OH^-, generating highly reactive $OH^{\bullet}$ radicals, which in turn attack any organic matter oxidizing it. At higher concentration of organic water pollutants direct oxidation of them by holes is also possible [14-16].

It can be added here that the process is conducted under normal (room-like) temperature and pressure conditions, the photocatalyst is wholly recovered after the process and its active surface is able to run the reactions again [17,18]. In contrast to other water purification methods, in the case of water contaminants containing only C, H and O atoms the heterogeneous photocatalytic processes do not introduce to the environment any additional impurities except CO_2 and H_2O.

The presented studies focus on identification of primary intermediates of glucose photooxidation on titania. However, first part of the paper is devoted to the possibility of glucose oxidation on illuminated TiO_2 – these studies were conducted in order to find the conditions, in which the degree of glucose degradation was small allowing thus determination of only partly oxidized products. The studies are a part of a broader research on purification of dairy sewage conducted since several years.

2. MATERIALS AND METHODS

Photochemical studies were conducted using solutions having various concentration of glucose. Depending on experiment, the concentrations of glucose-D(+) (99.5%, Aldrich) were as follows: 0.28, 0.40, 0.60, 0.80, 1.0 or 1.4 $g \cdot dm^3$. In the all photocatalytic experiments 230 cm^3 of an appropriate solution of glucose was mixed with 0.05 g TiO_2 (99.9%, Aldrich, anatase) and sonicated for 5 minutes. Then the homogenized slurry was transported to an air lift loop photoreactor (Pyrex made, 250 cm^3 volume) described elsewhere [19,20]. The photoreactor contents were mixed by an air lift (50 $cm^3 \cdot min^{-1}$) controlled by a narrow draft tube placed in the centre of the tube reactor. The conical bottom of the reactor was equipped with a septum through which the air stream was fed to the reactor with a needle, the loop of which reached the bottom of the draft tube. The reactor was illuminated from the side wall with two 300W xenon lamps (OSRAM). The bulbs were placed in a distance of 50 cm from the reactor, the distance between them was also 50 cm. Pyrex walls of the reactor determined lower limit of entering light (about 300 nm cutoff filter). The photoreactor was cooled by an air stream, the temperature was maintained at 30 ^{0}C.

Photocatalytic experiments were performed in a non-continuous mode (batch reactor); before each experiment the reaction slurry was aerated for 15 minutes. The photoreactions were conducted 3 hours, pH of illuminated solutions were measured at 30 minute intervals. After the illumination had been stopped, several cm^3 of the reaction

slurry (depending on initial glucose concentration) was analysed for COD using a dichromate method [21]. Each photocatalytic experiment was repeated at least twice, also each reaction solution (reaction slurry) was analysed for COD at least twice prior and after illumination. Direct glucose photolysis was also studied using the same reactor and light source.

Intermediates of the process of glucose photocatalytic degradation were identified using gas chromatography – mass spectroscopy techniques. Analyses were performed on a Varian GC/MS 4000 apparatus equipped with a capillary column VF – 5MS (30m·0.25mm·0.39mm). After three hour illumination the reaction slurry was filtered using Millipore Millex GV$_3$ filters and liquid phase was evaporated on a rotary evaporator to dryness. The residue was silanized 60 min at 70°C using TMSI – N-trimethylsilylylimidazole : pyridine = 1 : 4 (Sylon^{TM}TP, Supelco).

The water used for photocatalytic studies was doubly distilled in a quartz still. Prior to distillation the water was de-ionised on a special column. All chemicals were of p.a. purity. Anatase titania (99.9%, Aldrich) used as a photocatalyst had a BET specific surface area of 11.9 m^2·g^{-1} as measured on a Micromeritics apparatus. It showed a typical anatase spectrum with the adsorption onset at about 400 nm (taken on a Specord M-40 spectrophotometer). An average particle size of the TiO$_2$ powder was about 0.1 μm (89% of the particles were in the range 0.07 – 0.2 μm), as measured on a Malvern Instruments Ltd. (UK) granulometer using water as a liquid medium.

3. RESULTS AND DISCUSSION

As it was mentioned above, the goal of this study was to identify primary intermediates of glucose photocatalytic oxidation. However, prior to identification studies the conditions suitable for production of possibly large amount of primary products of the reaction of hydroxyl radicals, generated by illuminated titania, with glucose molecules were established. In these studies glucose oxidation was followed by determination of COD (Chemical Oxygen Demand) prior and after illumination of the solutions. Although time consuming, the COD dichromate method seemed to be the only one suitable for these studies - it was possible to determine at the same time the compounds present in water and adsorbed on titania grains (the slurry was not filtered). It was checked in blank experiments that the presence of small titania admixture did not influence the results of COD measurements. The results of previous studies conducted in this laboratory [22] were the base for setting of the reaction conditions: 230 cm^3 of the reaction solution, 0.05 g TiO$_2$, air stream rate 50 cm^3·min^{-1}. There were two reasons for the choice of glucose concentration: (1^0) possibility of production of only partly oxidized glucose derivatives, and (2^0) the fact, that at too high concentrations of organics in water the photoreaction rate could be substantially reduced or even totally

inhibited.

The results of three-hour illumination of diluted solutions, having various concentration of glucose, in the presence of TiO_2 photocatalyst are shown in Table 1.

Table 1. Degradation of glucose during three hour illumination of 230 cm^3 of the solution in the presence of TiO_2

Glucose initial concentration					Decrease of COD	
[g/dm^3]	[mmole/dm^3]	[Glucose contained in 230mL]			[%]	[mmole O$_2$]**
		[g]	[mmole]	[mmole O$_2$]*		
0.28	1.5	0.064	0.35	2.10	6.19	0.13
0.40	2.2	0.092	0.51	3.06	5.84	0.18
0.60	3.3	0.138	0.77	4.62	5.84	0.27
0.80	4.4	0.184	1.02	6.12	5.67	0.35
1.00	5.5	0.230	1.28	7.68	5.72	0.44
1.40	7.8	0.322	1.79	10.74	5.63	0.60

* amount of oxygen necessary for full oxidation of glucose contained on the photoreactor
** decrease of oxygen demand after three-hour illumination; the values correspond to the extent of oxidation reactions procceding in the reactor during illuminatiom

It follows from the data shown in Table 1 that three-hour illumination of glucose solutions with TiO_2 admixtures causes slow oxidation of the substrate. Moreover, quantitatively decrease of COD is directly proportional to its initial value, in other words – to initial concentration of glucose. Therefore, it can be assumed roughly, that the photocatalytic reaction fulfils universally applied Langmuir-Hinshelwood equation [14]. At too high concentrations of the degraded substrates, however, the kinetics of the process can change to zero order, because the reaction rate is limited by the rate of generation of $OH^{\bullet}$ radicals on the surface of illuminated titania, which is constant under constant illumination. In order to find real influence of the catalytic effect of illuminated TiO_2 it was of interest to study also direct glucose photolysis.

Table 2. Glucose degradation under illumination of glucose solution with and without TiO_2 admixture

Glucose concentration	Decrease of COD			
	With TiO_2 admixture		Without TiO_2 admixture	
[g/dm^3]	[%]	[mmole O$_2$]*	[%]	[mmole O$_2$]*
0.28	6.19	0.13	1.06	0.022
0.60	5.84	0.27	0.57	0.026
1.40	5.63	0.60	0.33	0.035

* see footnote below Table 1

The results are shown in Table 2; for comparison, the results obtained in the presence of TiO_2 are also inserted in Table 2.

One can see from Table 2 that the yield of direct glucose photolysis, which leads to oxidation, ranges from 6 to 17 % of that in the presence of TiO_2. The amount of oxidized glucose is somewhat higher at higher substrate concentration, although the increase is much smaller than that in the presence of TiO_2.

It was mentioned in *Experimental* that during the photocatalytic reactions, pH of the slurry was measured at 30 minute intervals. In the case of all photocatalytic reactions, lowering of pH was observed with the time of illumination. For reactions conducted in the presence of illuminated TiO_2 the pH values lowered during three-hour reaction from initial pH 6.5 - 6.8, depending on glucose concentration, to 4.5 - 4.8. As an example Fig.1 shows the changes of 1.0 g·dm^{-3} glucose solution in the presence of TiO_2.
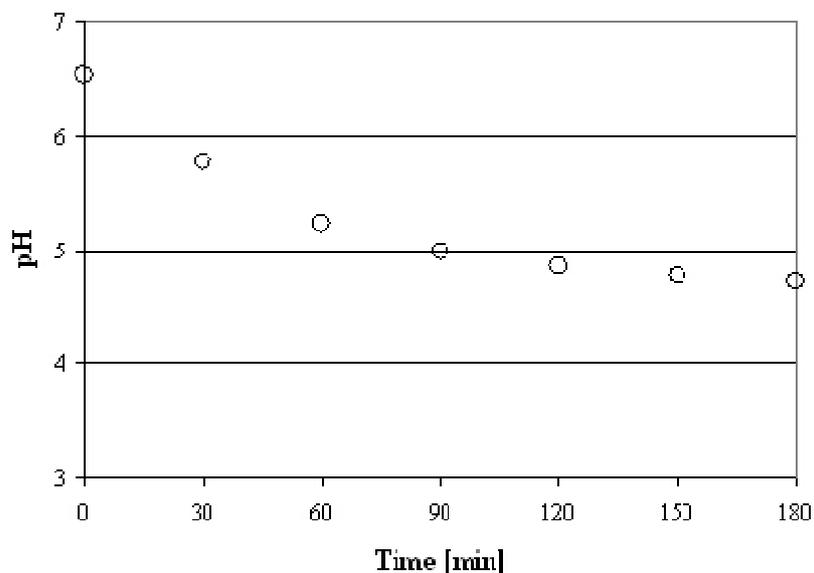

Fig. 1. pH changes during 3-hour illumination of 1.0 g dm^{-3} glucose solution in the presence of TiO_2.

The formation of acidic intermediates is not surprising. According to literature, oxidation of water contaminants in the presence of illuminated titania proceeds *via* formation of OH˙ radicals, direct oxidation by electron holes can take place in the cases of highly concentrated water solutions. Also strong adsorption of the compound on TiO_2 facilitates its direct oxidation by the holes [15,16]. The attack of OH˙ radicals on hydroxylated carbon atom in sugar leads firstly to formation of a new carbonyl group.

The reaction of OH$^{\bullet}$ with the carbonyl group (the already existing or the new formed) causes formation of a carboxyl group. If the CO group is non-terminal, the brake of a carbon chain and formation of two new compounds are observed. Therefore, although the oxidation in the presence of illuminated TiO$_2$ leads finally to CO$_2$ and H$_2$O, a lot of various intermediates are formed in the one-electron processes caused by OH$^{\bullet}$ radicals. And reactions of formation of acidic compounds and their next decarboxylation are necessary in the whole process of mineralization of organic compounds.

pH changes illustrated in Fig.1 show, that the photoreaction still proceeds during the whole period of illumination. However, the pH decrease, fast during first 90 minutes, becomes slower and slower in the next period, *i.e.* when pH of the slurry decreases below 5.
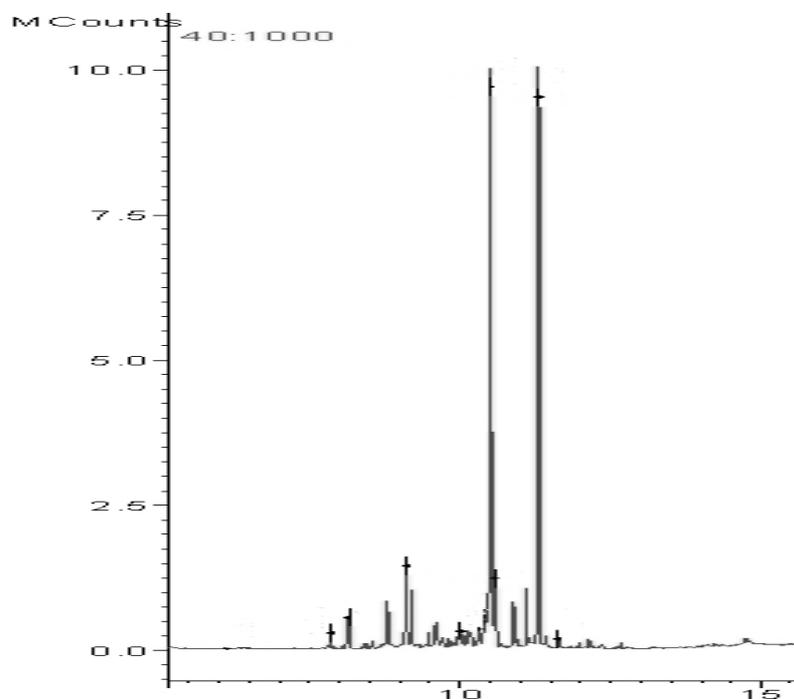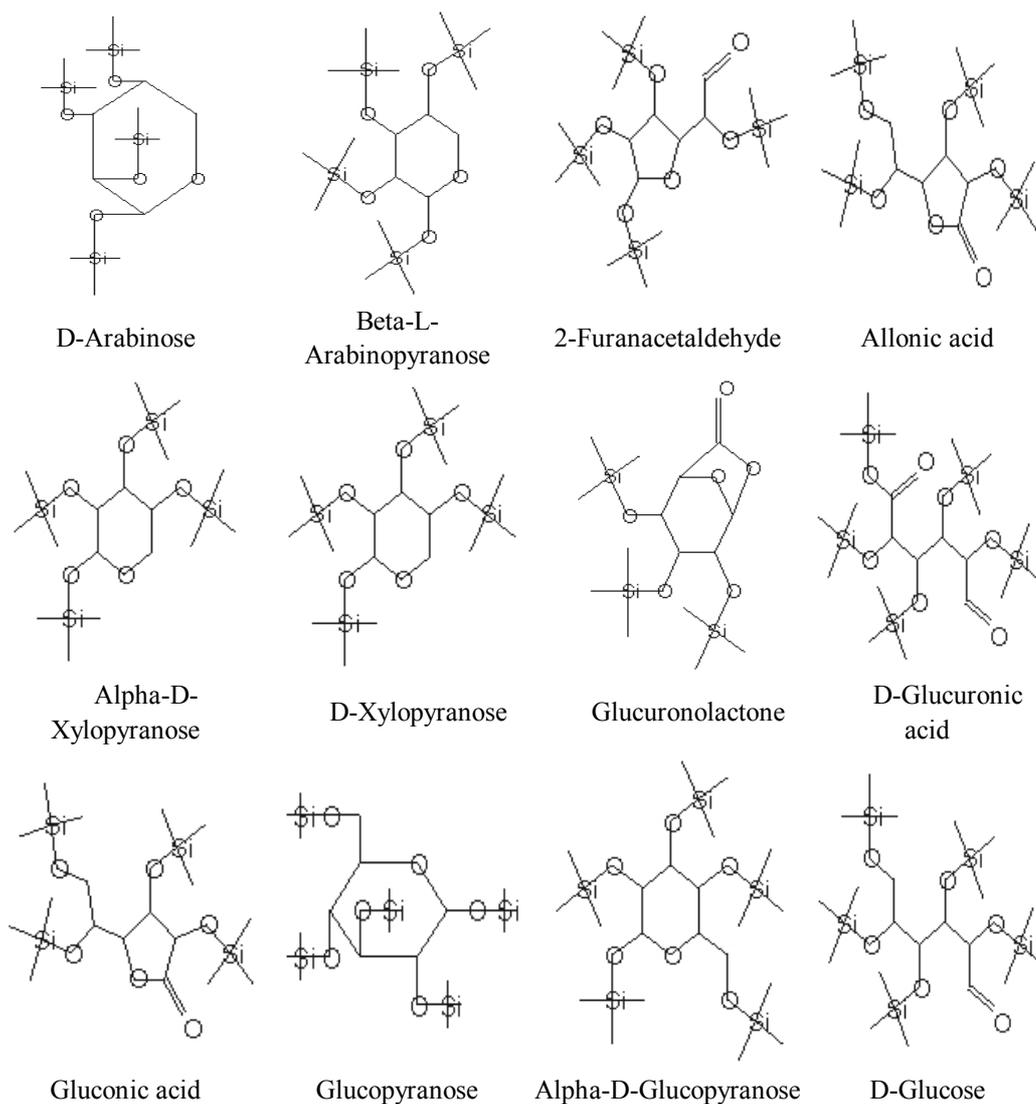

Fig. 2. GC-MS chromatogram of an after reaction mixture. Glucose concentration, 0.4 g·dm^{-3}, time of illumination, 3 hours; amount of titania, 0.05 g.

Intermediates of glucose oxidation on illuminated titania were determined using GC-MS technique. Prior to analysis 0.4 g·dm^{-3} aqueous glucose solution was illuminated 3 hours in the presence of TiO$_2$, filtered, dried, and dry residue was silanized (see *Experimental*). Typical GC-MS chromatogram is shown in Fig.2.

MS analysis of the after-reaction mixture ingredients showed the existence of many intermediate compounds, which were formed both as a result of intramolecular changes and oxidation reactions. Formulas of the derived compounds (their silanized derivatives) are collected below, see Fig.3.

D-Arabinose	Beta-L-Arabinopyranose	2-Furanacetaldehyde	Allonic acid
Alpha-D-Xylopyranose	D-Xylopyranose	Glucuronolactone	D-Glucuronic acid
Gluconic acid	Glucopyranose	Alpha-D-Glucopyranose	D-Glucose

Mannose   Mannonic acid   D-Ribofuranose   Inosose-2
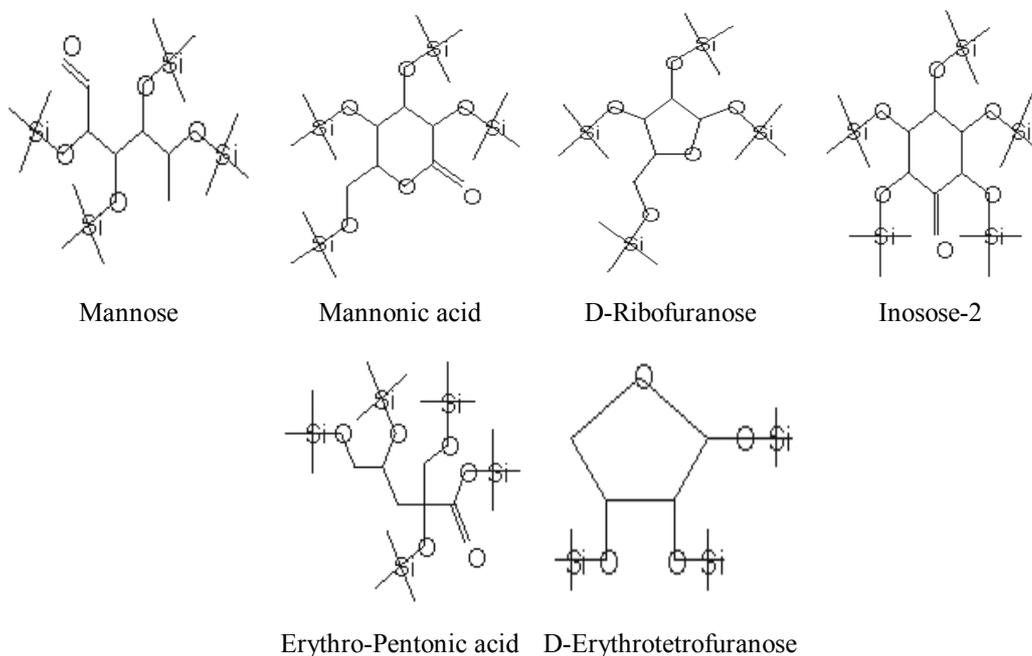
Erythro-Pentonic acid   D-Erythrotetrofuranose

Fig. 3. Formulas of silanized derivatives of the compounds determined by GC-MS.

The highest peaks in Fig.2 correspond to the next compounds in the order: glucopyranose>glucose>gluconic acid>2-furanacetaldehyde>allonic acid. Note, that acidic derivatives were indeed formed during the photocatalytic reaction confirming thus the results of pH measurements. And two of the acids, *i.e.* the gluconic and allonic ones, gave the most intensive peaks among the oxidized intermediates. The formation of glucose derivatives in the way of intramolecular transformation can be a result of both pH changes and catalytic action of titania surface, acidic in principle. The research is in progress in order to establish the main direction of glucose oxidation by the photogenerated OH$^\bullet$ radicals and to determine also the shorter chain intermediates.

4. CONCLUSIONS

Illumination of glucose diluted solutions in the presence of TiO$_2$ leads to oxidation of the substrate. In the range of concentration 0.20-1.40 g·dm^{-3} the yield of glucose degradation, measured as a decrease of COD, was small and amounted to 5.8%. It was assumed, that the reaction shows 1st order behaviour. During illumination pH of the reaction solutions lowered showing thus formation of acidic intermediates. GC-MS analysis, conducted after silanization of the reaction products, showed the existence of

many intermediate compounds, both these formed in result of intramolecular changes, and these formed by glucose oxidation. Acidic compounds such as: gluconic acid, D-glucuronic acid, mannonic acid, erytho-pentonic acid and the allonic one were found as reaction intermediates. Two of the acids, i.e. gluconic and allonic ones, gave the most intensive peaks among the intermediates.

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