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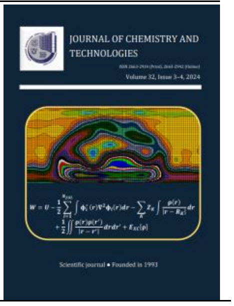

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THE DEGRADATION OF D-GLUCOSE IN ACIDIC AQUEOUS SOLUTION

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Abstract

The objective of this work was to estimate glucose degradation products (GDPs) in model system D-glucose/H^+ based on the changes in the pH values, absorption of ultraviolet (UV) light and integral intensities of carbonyl absorption (*ν* 1740–1710 cm^{-1}) by Raman spectroscopy. Spectrophotometric, pH-metric and Raman spectroscopy methods were used to elucidate mechanism of both glucose degradation and transformation of GDPs in the model D-glucose solutions after desired time and temperature of heating. Common features for all the tested solutions after heating were reduce in pH values and increase in UV absorbance at λ_{max} 225 *nm* (absorbance of 3,4-DGE) and in the carbonyl region λ_{max} 280-285 *nm* (absorbance of 5-HMF). This indicated that these intermediates had been formed during heating. Their stability increases with a decrease in initial pH values. By Raman and UV spectroscopy methods temperature zones were determined in which certain processes of transformation of D-glucose were seen. It was demonstrated that in the temperature interval at 80–95 °C at all pH values, formation of 3,4-DGE accelerated while the their transformation into 5-HMF slowed down. It was shown that the formation of unsaturated carbonyl-containing compounds (3,4-DGE), as starting intermediates for further transformations were slowed down at pH 3, which indicates a certain stability of D-glucose under these conditions.

Keywords: glucose; glucose degradation products; 3,4-di-deoxyglucosone-3-ene; 5-hydroxymethylfurfural; acidic compounds.

ПЕРЕТВОРЕННЯ D-ГЛЮКОЗИ У КИСЛОМУ ВОДНОМУ РОЗЧИНІ

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Анотація

Метою цієї роботи була оцінка продуктів розпаду глюкози (GDP) у модельній системі D-глюкоза/H^+ на основі змінення значень pH, поглинання ультрафіолетового (УФ) світла та інтегральних інтенсивностей поглинання (КР спектроскопія) у карбонільній області (ν 1740–1710 $см^{-1}$). Спектральні методи і pH-метрія були використані для з'ясування механізму як деградації глюкози, так і трансформації GDP у модельних розчинах D-глюкози після дії завданого часу та температури нагрівання. Загальними ознаками для всіх досліджуваних розчинів після нагрівання були зниження значень pH і збільшення УФ-поглинання за λ_{max} 225 нм (поглинання 3,4-DGE) і в карбонільній області λ_{max} 280–285 нм (поглинання 5-HMF). Це вказує на те, що ці проміжні продукти утворилися під час нагрівання. Їх стабільність підвищується зі зниженням початкових значень pH. Методами раманівської та УФ-спектроскопії визначено температурні зони, в яких спостерігаються певні процеси перетворення D-глюкози. Показано, що в інтервалі температур 80–95 °C за всіх значеннях pH прискорюється утворення 3,4-DGE, а їх перетворення в 5-ГМФ сповільнюється. Показано, що утворення ненасичених карбонілвмісних сполук (3,4-DGE) як вихідних інтермедіатів для подальших перетворень, сповільнюється за pH 3, що свідчить про певну стабільність D-глюкози за цих умов.

Ключові слова: глюкоза; продукти розпаду глюкози; 3,4-ди-дезоксиглюкозон-3-ен; 5-гідроксиметилфурфурол; кислотні сполуки.

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Introduction

Glucose is widely used as a raw material for both simple food products and complex industrial food systems [1–4]. In medical practice, glucose is still used in the composition of solutions for dialysis and these solutions are undergone heat sterilization [5–6]. The degradation of D-glucose is a whole set of reactions that typically occur during heat processing. This process gives rise to forming glucose degradation products (GDPs) including 3,4-dideoxyglucone-3-ene (3,4-DGE), 5-hydroxymethylfurfural (5-HMF), acetaldehyde, formaldehyde, methylglyoxal, glyoxal, low molecular acids and other compounds [7–15]. Some of the formed products have a certain smell and its can give the food product both a desirable and undesirable aroma [16–18].

Consequently, in the processes which GDP provides the necessary aroma, it is necessary to select such optimal conditions for the processing of food products, so that these components can be used to their full extent. And in processes which this reaction is undesirable, it is necessary to reach a compromise between the minimization of GDP formation and the conditions of food processing.

The level of both the glucose degradation and transformation of GDPs depend on the initial pH values, time and temperature of heating during food processing [19–21].

Spectrometric and pH-metric methods are simple, rapid and cheap to allow investigation of formation of intermediates in the early stage of D-glucose degradation under different conditions (pH, temperature). Furthermore, these methods predict possible mechanisms of glucose degradation in a particular solution.

In this work, the changes in both the pH values and spectral characteristics of D-glucose solutions after desired time and temperature of heating have been investigated.

Materials and Methods

Chemicals

Laboratory-made glucose solutions of model system D-glucose/H^+ sample 1 contained 1 *mol/l* of D-glucose, sample 2 contained 3.5 *mol/l* of D-glucose, sample 3 contained 2 *mol/l* of D-glucose. Appropriate pH values were adjusted with HCl. Laboratory-made solutions were heated at desired temperature for various times.

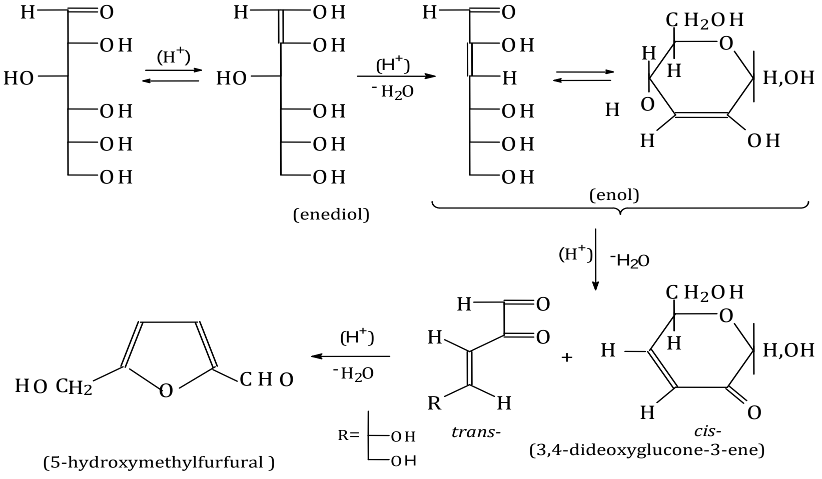
Instruments

Spectrophotometer Photometry Hitachi U2810 (Hitachi High-Technologies Corporation, Japan) was used. pH values were determined by pH meter XS Instruments DHS Basic (50001202, Italy). Raman spectrometer ReactRaman (Mettler Toledo, Switzerland) was used.

Results and Discussion

Initial reaction intermediates in model systems of glucose/H^+ formed through Lobry de Bruyn-Alberda van Ekenstein transformation reactions (1,2- and 2-3-enolization of reducing sugars to enediols). Further dehydration of these products is responsible for the formation of enol and its hemiacetal via β-elimination reactions. Subsequent elimination of water helped formation of 3,4 -dideoxyglucone-3-ene (unsaturated ozone), *trans*- and *cis*-forms, respectively. It has been proven that *trans*-3,4-dideoxyglucone-3-ene is the most reactive intermediate, which in acidic media is transformed into carbonyl-containing compounds (Scheme) and acidic compounds [22].

By monitoring the formation of intermediates in the early stage of D-glucose degradation under different conditions (pH, temperature) it is possible to deduce which directions dominate under the given, clearly defined reaction conditions.



Scheme 1. Conversion of D-glucose into intermediate compounds

In order to determine the differences in the formation of intermediate compounds, model solutions of D-glucose (1 mol/l) [sample 1] at a pH range between 3.0 and 7.0 were studied after heating in a water bath for varying heating times.

The two detection wavelengths of ultraviolet (UV) absorption selected for this study were λ_{max} 225 nm and λ_{max} 280–285 nm. The absorbance at λ_{max} 225 nm is mainly due to unsaturated carbonyl-containing compounds, including 3,4 - dideoxyglucone-3-ene (3,4-DGE). The absorbance at λ_{max} 280–285 nm indicates the formation of carbonyl-containing compounds, including 5-hydroxymethylfurfural (5-HMF). Changes in both the initial pH values and the absorbance at λ_{max} 225 and λ_{max} 280-285 *nm* of D-glucose solutions were monitored.

After 5 hours heating all solutions showed two absorption maxima at 225 nm and 280–285 nm with different ratios to each other (Table 1). The formation of intermediate 3,4-DGE with λ_{max} 225 *nm* prevailed at a pH range between 3.0 and 5.0. The solution with pH 3.0 showed almost equal ratio of two absorption maxima, and at pH > 5.0 the formation of intermediate 5-HMF with λ_{max} 280–285 nm prevailed largely.

Table 1

The influence of pH on the formation of intermediates in the early stage of D-glucose degradation (1 mol/l, H_2O, 95 °C, 5 h.)

Initial pH values	$O.D._{\lambda max 225\ nm}$	$O.D._{\lambda max 285\ nm}$	$\frac{O.D._{\lambda 225нм}}{O.D._{\lambda 280нм}}$	Final pH value
3.0	0.30	0.30	1	3.0
5.0	0.39	0.40	1.18	4.2
7.0	0.48	0.55	0.87	5.3

The formation of carbonyl-containing compounds, including 5-HMF, is observed at pH 3.0 in the smallest extent. This means that this concentration of hydrogen ions ensures the stability of D-glucose and does not helped formation of the (di)carbonyl compounds as a starting intermediates for further transformations.

Therefore, it can be postulated that initial pH values (concentration of hydrogen ions) possibly determines two directions of the D-glucose degradation in acidic solutions.

1. In weakly acidic D-glucose solutions (values pH between pH 5.0 and 7.0) the formation of reactive unsaturated carbonyl-containing intermediates, including unsaturated ozone (3,4-DGE) and 5-HMF is accelerated for 5 hours heating. Hydrogen ions catalyze the formation of an enediol structure and subsequent dehydration reactions, but minimize possible aldolization reactions of (di)carbonyl compounds. That's probably why reactive intermediates (3,4-DGE) and 5-HMF can be fixed in acidic solution.
2. In strongly acidic D-glucose solutions (initial pH value 3.0) the formation of acidic compounds noticeably accelerates. According to common assumptions the enediol, possibly via keto–enol tautomerization and followed by a benzilic acid rearrangement converted into acids [23; 24].

It was determined that temperature significantly accelerates degradation process of reducing sugars [25; 26]. In order to fix certain stages in the rapid sequence of reactions of the degradation of reducing sugars, solutions of D-glucose at different temperatures were investigated.

D-glucose solutions (3.5 mol/l) [sample 2] at pH values 1.0, 3.0, 5.0 after heating for 30 minutes at desired temperatures (20 °C, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, 95 °C) were studied.

The effect of temperature on the formation of carbonyl-containing intermediates in the early stage of D-glucose degradation were examined by Raman spectroscopy.

D-glucose solutions absorb in the carbonyl region of 1740–1710 cm^{-1} and these bands were assigned to 3-*keto*, 2-*keto* and *aldehyde* forms of the sugars, respectively, formed through Lobry de Bruyn-Alberda van Ekenstein transformation reactions [20].

Changes in the integral intensities of carbonyl absorption (ν 1740–1710 cm^{-1}) of D-glucose solutions as a function of temperature and pH (Fig.1) clearly indicated the sequence of at least three processes in the early stages of D-glucose degradation.

1. In the temperature interval at 20–60 °C at all pH values, a rapid increase in carbonyl absorption intensities is observed, which can be explained by an increase in the concentration of carbonyl forms in tautomeric transformations of D-glucose.
2. In the temperature interval at 60–80 °C at a pH range between 3.0 and 5.0 the intensity of the carbonyl band was diminished, indicating the transformation of acyclic forms (carbonyl and enediol).

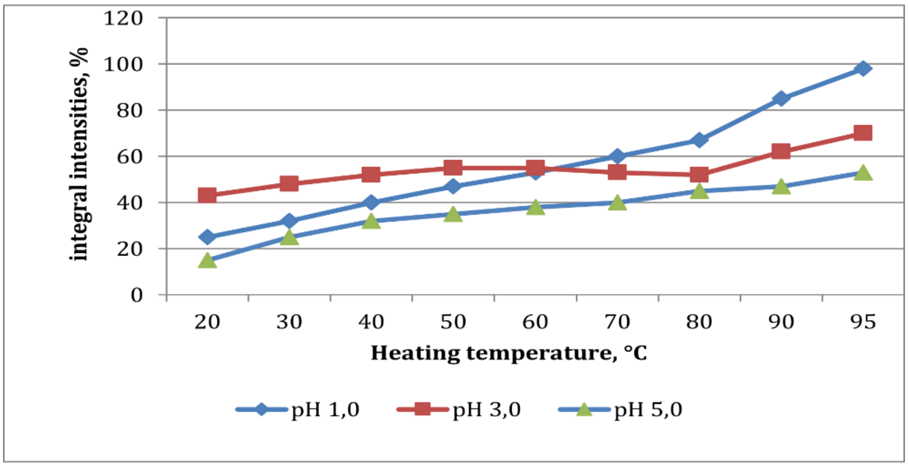


Fig 1.The effect of temperature on the formation of carbonyl-containing intermediates (ν 1740-1710 см⁻¹) in the early stage of D-glucose degradation (3,5 mol/l, H_2O, 30 min)

3. In the temperature interval at 80–95 ° at all pH values, the intensity of the carbonyl absorption bands increases again, which means the formation of (di)carbonyl intermediate compounds in the rapid transformations of unstable and reactive intermediates of the previous stages (fig.1).

This assumption is in agreement with UV spectral studies. The D-glucose degradation was studied in the solutions (2 mol/l) [sample 3] at a pH range between 3.0 and 7.0 at desired temperatures (50 °C, 60 °C, 70 °C, 80 °C, 95 °C) after 3 hours of heating. The formation of the corresponding intermediates was monitored for each initial pH value by both absorption at λ_{max} 225 nm (fig.2) and λ_{max} 280–285 nm (fig.3) and change in the pH values (fig.4) as function of heating temperature.

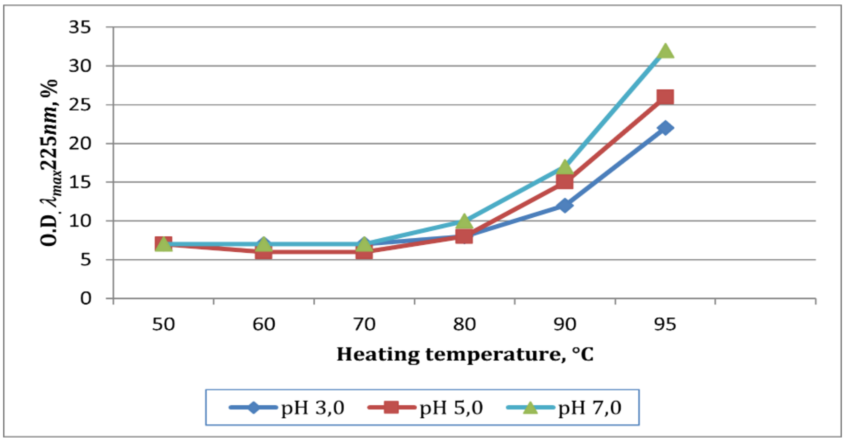


Fig 2. Change in optical density O.D. λ_{max}225nm of D-glucose solutions as function of heating temperature (2 mol/l, H_2O, 3 hours)

Here, two temperature zones can be distinguished which two different transformation processes take place.

1. In the temperature interval of 50–80 °C at pH range between 3.0 and 7.0 very weak, almost stable absorbance at λ_{max} 225 nm and λ_{max} 280–285 nm is observed for each initial pH value. In this temperature range, the pH value drops and the more strongly, the higher it was in the beginning. Only the initial pH values 3.0 remained stable at desired temperatures. It is tempting to speculate, however, that in this temperature interval at pH range 7.0 acid formation processes actively prevail. These processes slow down when the concentration of hydrogen ions increases and are not observed in strongly acidic solutions.

2. In the temperature interval at 80–95 °C at all pH values, the absorbance at λ_{max} 225 nm and λ_{max} 280–285 nm increases intensively, especially at λ_{max} 225 nm. Such observations allow to assume

that in this temperature range there is a rapid and predominant formation of unsaturated carbonyl-containing intermediate compounds with λ_{max} 225 nm (possibly 3,4-DGE) and a slower increase in the concentration of carbonyl-containing intermediates with λ_{max} 280-285 nm (including 5-HMF).

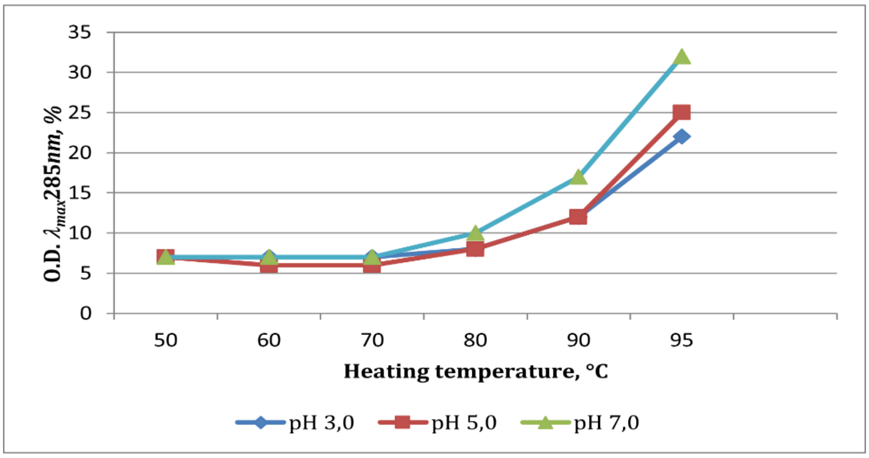


Fig 3. Change in optical density O.D. *λ*λ_{max} 285 nm of D-glucose solutionsas function of heating temperature (2 mol/l, H_2O, 3 hours)

Comparing the changes in the D-glucose/H^+ reaction system, over the entire range of acidic pH values, it can be stated that at pH 3.0, all processes occurring in the early stages of the acid decomposition reaction are noticeably slowed down.

It is tempting to assume that in this temperature range at pH 7.0 acid formation processes actively prevail.

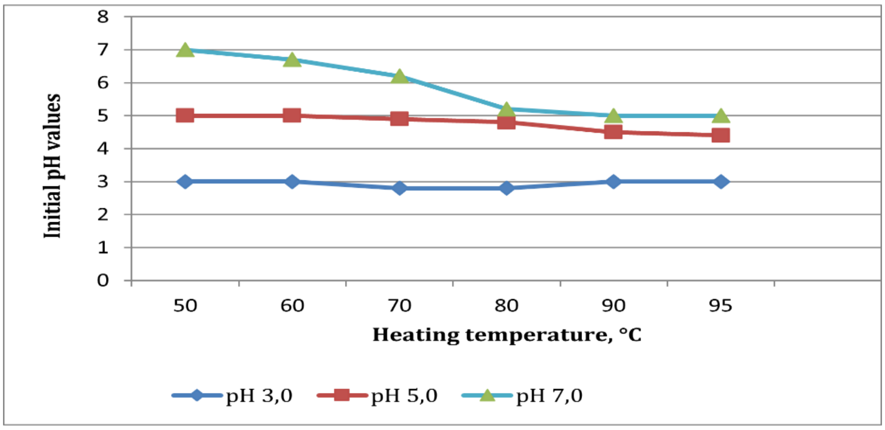


Fig 4. Change in the *pH* values of D-glucose solutions as function of heating temperature (2 mol/l, H_2O, 3 hours)

Conclusion

Glucose degradation and converting of GDPs occur during the thermal processing of food. Simple and rapid UV spectrometric, potentiometric and Raman Spectroscopy methods have potential to estimate transformation processes in acidic solutions of D-glucose during their heating.

We have confirmed that the concentration of hydrogen ions affects the course of the early stage of the glucose degradation reaction. The formation of intermediate compounds may be estimated by quick measurement of pH, the absorbance of 3,4-DGE at λ_{max} 225 nm and 5-HMF at λ_{max} 280–285 nm, respectively. In the temperature interval at 50–80 °C at acidic values of pH slight almost stable formation of 3,4-DGE and 5-HMF was observed. At the same time the pH value drops and the more strongly, the higher it was in the beginning. It can be assumed that in this temperature interval at pH 7.0 formation of acidic compounds actively prevail. These processes slow down when the concentration of hydrogen ions increases and are not observed in strongly acidic solutions. In this temperature range there is both a rapid and predominant formation of 3,4-DGE and a slower increase in the concentration of 5-HMF.

In conclusion, the sequence of at least three processes in the early stages of D-glucose degradation is presented on the base of own studies and literature data.

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