

---

## NUTRITIONAL SCIENCE

---

DOI: <https://doi.org/10.23649/jae.2020.2.14.2>

Cherepanov I.S. \*

Udmurt State University, Izhevsk, Russia

\* Corresponding author (cherchem[at]mail.ru)

Received: 09.04.2020; Accepted: 29.04.2020; Published: 24.06.2020

### ACETALS AND ETHERS FORMATION DURING ACID-CATALYZED GLUCOSE'S CARAMELIZATION

Discovery note

#### Abstract

The present paper has studied the formation of acetals in acid catalyzed caramelization processes in ethanol medium, showed an increase in hydrophobic properties of acetalized products, confirmed calculations of lipo-hydro partition coefficient values. It is possible, that the hydrophilic OH-groups are also bonded by the solvent molecules into ethers. Based on the data obtained, it can be concluded that it is possible to hydrophobize caramel compositions when they are synthesized in acidic ethanolic media, which allow to develop technological compositions based on simple carbohydrates in the future.

**Keywords:** D-glucose, caramels, IR-Fourier transform spectroscopy, structure, acetals, ethers

Черепанов И.С. \*

Удмуртский государственный университет, Ижевск, Россия

\* Корреспондирующий автора (cherchem[at]mail.ru)

Получена: 09.04.2020; Доработана: 29.04.2020; Опубликовано: 24.06.2020

### ОБРАЗОВАНИЕ АЦЕТАЛЕЙ И ЭФИРОВ В ПРОЦЕССАХ КИСЛОТНО- КАТАЛИЗИРУЕМОЙ КАРАМЕЛИЗАЦИИ ГЛЮКОЗЫ

Краткое сообщение

#### Аннотация

В настоящей работе изучено образование ацеталей в процессах кислотно-катализируемой карамелизации в этанольной среде, показано увеличение гидрофобных свойств ацеталированных продуктов, подтвержденное расчетов значений коэффициентов распределения. Вероятно, параллельно с ацетализацией протекают процессы связывания гидрофильных OH-групп в простые эфиры. По результатам проведенных исследований можно сделать вывод о возможности гидрофобизации карамельных составов при их синтезе в кислых этанольных средах, что позволит в дальнейшем разрабатывать технологические составы на основе простых углеводов.

**Ключевые слова:** D-глюкоза, карамели, ИК-Фурье спектроскопия, структура, ацетали, эфиры.

#### 1. Introduction

Carbohydrate thermal degradation products have a complex non-uniform structure, research of which is of considerable interest for food chemistry and technology, agricultural industry, besides, caramels are widely used as natural dyes [1]. Modification of caramelized carbohydrates allows to obtain synthetic analogues of natural substances, as well as new high-molecular products [2]. Surface properties of caramels, their adhesion and emulsification depend on the nature of the functional groups [1]. Caramel colors contain carbohydrate and furan ring skeletons as well as a large number of hydroxyl, carboxyl and aldehyde groups, which gave them good hydrophilicity [3]. High functionalization of caramels allows different reactions to be used to modify them, which leads to a change in properties. In particular, most caramels hardly dissolve in the oil phase or grease products, and authors [3] show the possibility of hydrophobizing caramels by acylation by higher acid halides, which proposes their application in oil-containing foods or oil products. The lipid-water partition coefficient (P) and its rair value (log P) are important indexes for the hydrophilic properties of a compounds [3]. Liquid-phase caramelization is the more condition-light reaction compare to dry caramelization processes (the higher temperature leads to lower moisture content) and also allows to provide some reactions. One of the methods of modification by carbonyl functions is acetalization [4], semi-acetals and acetals in food systems are practically important as taste and aroma components, therefore the processes of acetal formation in acid catalytic caramelization of glucose in ethanol medium are studied in present paper.

## 2. Methods

The products were synthesized by thermostating under reflux of ethanol solutions (EtOH 96% "Merck") containing 0.002 moles of *D*-glucose in 25 ml of solvent in the presence of  $3 \cdot 10^{-4}$  moles of  $H_2SO_4$  and  $NH_4Cl$  during 1 hour. Electron absorption spectra of diluted samples (1:5) of solutions were collected in quartz cuvettes in the wavelength range of 200-600 nm on a SF-2000 spectrophotometer (OKB Spectr, St. Petersburg, Russia). Product isolation was carried out by removing the solvent under reduced pressure, washed by diethyl ester and dried. The spectra of solid products were taken in the transmission format in KBr tablets (1:250) on FSM 2201 FT-IR spectrometer (InfraSpek LLC, St. Petersburg, Russia) in wave interval figures of  $4000-400\text{ cm}^{-1}$  with a spectral resolution of  $4\text{ cm}^{-1}$  at 16 to 30 scans, the baseline was approximated by a 4-order polynomial. The original and second derivative spectra were processed in FSpec program. The values of lipo-hydro partition coefficients ( $\log P$ ) in the octanol-water system were determined according to the procedure [3].

## 3. Results

The process of forming the structure of caramels is a complex set of series-parallel reactions, the main structural elements of the final products are the non-organic chromophore fragments together with oxygen-containing functions and the aliphatic part of the structure [2], [3]. A maximum of 285 nm is recorded in the electron spectrum (Fig. 1), which corresponds to absorption of carbonyl groups of caramelization products, and its intensity is reduced, probably due to reaction with ethanol to form acetals, which is further confirmed by low absorption value in the region  $1700-1720\text{ cm}^{-1}$  (shoulder) in IR spectra (Fig. 2).

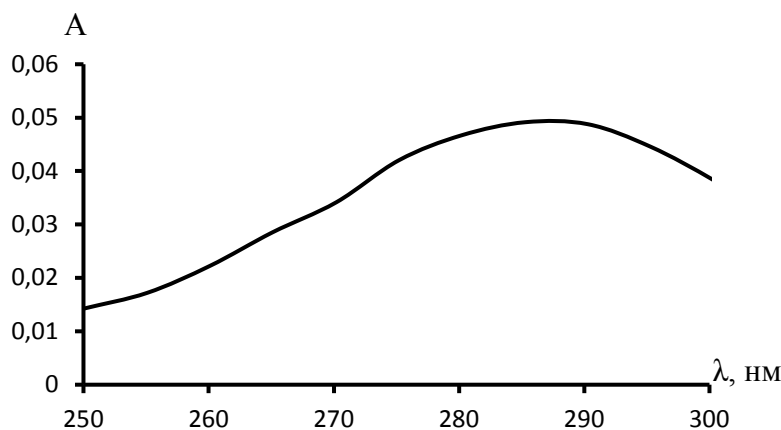


Figure 1 – Absorption spectra of caramel's ethanolic solution

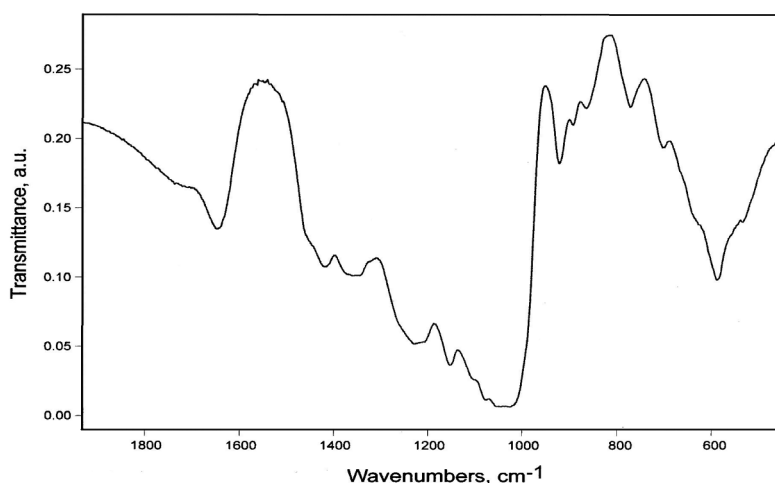


Figure 2 – IR-Fourier transform spectra of acidic D-glucose caramel

IR-Fourier transform spectra of isolated solid products in the region of  $900-1200\text{ cm}^{-1}$  are weakly resolved (Fig.2), therefore structural-group analysis was carried out using the method of the second derivatives (Fig. 3).

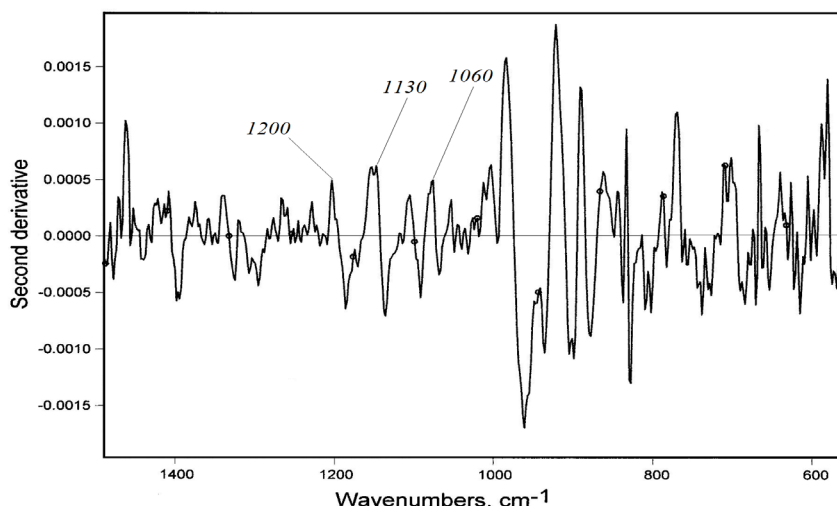


Figure 3 – Second derivative of IR Fourier transform spectra of D-glucose caramelization product

In second derivative spectra the bands at 1060, 1130 ( $\nu_{\text{OCO}}$ ) and 1200 ( $\nu_{\text{CCO}}$ )  $\text{cm}^{-1}$  are accurately fixed and characteristic of acyclic acetals [5], a bands at 813, 770 ( $\gamma_{\text{C-H}}$ ) and 1008 ( $\nu_{\text{COC}}$ )  $\text{cm}^{-1}$ , characteristic of furan ring confirms preservation of heterocycle. Carbohydrate ring vibrations are proved by the strong bands registration in region of 800-1020  $\text{cm}^{-1}$  and it is also possible, that the hydrophilic OH-groups are bonded into ethers [6], [7]. In second derivative spectra (Fig.3) bands of various intensity are found in this region (950, 915, 870, 852  $\text{cm}^{-1}$ ). These bands are interpreted as due to mixed CCH deformation vibrations coupled with CCO, OCO and COC bending. Both the number and frequencies of the bands in anomeric IR range depend on the conformation of the glucopyranose units. It is well known that the glucopyranose units exist in the six typical conformations (1C, C1, 1B, B1, 3B, B3) [8]. Bands at 915 and 852  $\text{cm}^{-1}$  indicate that the carbohydrate rings are presented in caramel structure as C1 “chair” conformation (one band in the region between 925 to 885  $\text{cm}^{-1}$  and another one around 860 to 820  $\text{cm}^{-1}$ , which are assigned to axial (A)-axial (A) and equatorial (E)-axial (A) mixed CH deformation vibrations respectively). Band at the 870  $\text{cm}^{-1}$  is considered as a characteristic for the changing of C1 conformation (EAAAA) to 3B (AAAAE) structure and some units are presented in final product’s structure as “boat” conformation. There is no signal in IR spectra at 1108  $\text{cm}^{-1}$ , ascribed to the asymmetric vibration of the C-OH bond at the C<sub>4</sub>-position of glucopyranose units [8], absence of this band suggests about bonding C<sub>4</sub>-O-H fragment. Changes in 1500-1300  $\text{cm}^{-1}$  region show the specific of bending vibrations of CH-OH groups and their rotating, but detailed analysis of  $\delta_{\text{CH}}$  and  $\delta_{\text{OH}}$  position and assignment is not clear accurate.

Part of structure fragment may be presented as a result of acid-catalyzed condensation of D-glucose and destruction product (5-hydroxymethylfurfural) [2], [9] (Fig. 4):

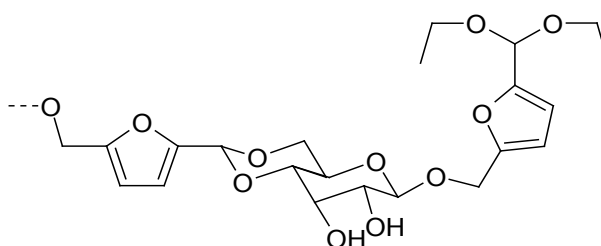


Figure 4 – Caramelized glucose’s structural fragment

Formation mechanism may be presented as a set of parallel condensation processes [9]. Comparison of lipo-hydro partition coefficients values of the isolated solid product ( $-0.10 \pm 0.05$ ) with logP obtained by authors [3] for lipophilic caramels (from -0.42 to 0.70) makes it possible to conclude the marked hydrophobic properties imparted to caramels during acetalization during synthesis in ethanol medium; further investigation allows to choosing experimental conditions for optimal synthetic caramel preparation.

#### 4. Conclusion

Carbohydrate caramels are one of the most important products, but caramelization manufacturing processes assume some problems due to sticky nature of caramels, such as adhesion to material surface, meaning that it is hard to remove caramel products from it. Based on the data obtained, we can conclude that it is possible to hydrophobize caramel compositions when they are synthesized in acidic ethanol media, containing ammonium salts, which allow to develop technological compositions based on simple carbohydrates in the future.

#### Conflict of Interest

None declared.

#### Конфликт интересов

Не указан.

### References

1. Surface characterization caramel at the micrometer scale / D. Morton, C. Roberts, M. Hey et al // J. Food Sci. - 2003. – Vol. 68. – P. 1411–1415.
2. Черепанов, И.С. К вопросу о возможности связывания биоактивных ариламинов продуктами термодеструкции углеводов / И.С. Черепанов // Хранение и переработка сельхозсырья. - 2018. – №1. – С.23–27.
3. Preparation and characterization of acylcaramels / Y. Geng, Y. Ning, Q. Shao et al // J. Agric. Food Chem. - 2019. – Vol. 67. – P. 5614–5620.
4. Chernyak, M. Preparative synthesis of furfural diethyl acetal through the direct interaction of alcohol and aldehyde / M. Chernyak, V. Tarabanko, A. Morozov, A. Kondrasenko // Journal of Siberian Federal University. Chemistry. - 2016. – Vol. 9. – P. 146–151.
5. Клыков, В.Н. Синтез природных 3-О-(1-алкенил)холестеринов / В.Н. Клыков, И.Ю. Михайлова, Г.А. Серебренникова, Р.Г. Евстигнеева // Биоорганическая Химия - 1979. – Т. 5. – С. 918–922.
6. Hu, X. Reaction pathways of glucose during esterification: effect of reaction parameters on the formation of humin type polymers / X. Hu, C. Lievens, A. Larcher, C.-Z. Li // Biores. Technol. – 2011. – Vol. 102. – P. 10104–10113.
7. Liu, J. Conversion of fructose into 5-hydroxymethylfurfural (HMF) and its derivatives promoted by inorganic salts in alcohol / J. Liu, Y. Tang, K. Wu // Carbohydr. Res. – 2012. – Vol. 350. – P. 20–24.
8. Nolic, G. Deconvoluted Fourier-transform LNT-IR study of coordination copper (II) compounds with dextran derivatives / G. Nolic, M. Cakic, Z. Mitic, L. Ilic // Rus. J. Coord. Chem. – 2008. – Vol. 34 – P. 322–328.
9. Formation, molecular structure, and morphology of numins in biomass conversion: influence of feedstock and processing condition / I. van Zandvoort, Y. Wang, C. Rasrendra et al // ChemSusChem. – 2013. – Vol. 6. – P. 1745–1758.

### References in English

1. Surface characterization caramel at the micrometer scale / D. Morton, C. Roberts, M. Hey et al // J. Food Sci. 2003. – Vol. 68. – P. 1411–1415
2. Cherepanov, I.S. K voprosu o vozmozhnosti svyazyvaniya bioaktyvnykh arilaminov produktami termodestruktsii uglevodov [To the problem of possibility of bioactive arylamines binding by the carbohydrate's termodestruction products] / I.S. Cherepanov // Khraneniye I pererabotka sel'khozsyriya [Storage and Processing of Farm Products] - 2018. – №1. – P.23–27. [in Russian]
3. Preparation and characterization of acylcaramels / Y. Geng, Y. Ning, Q. Shao et al // J. Agric. Food Chem. 2019. – Vol. 67. – P. 5614–5620.
4. Chernyak, M. Preparative synthesis of furfural diethyl acetal through the direct interaction of alcohol and aldehyde / M. Chernyak, V. Tarabanko, A. Morozov, A. Kondrasenko // Journal of Siberian Federal University. Chemistry. - 2016. – Vol. 9. – P. 146–151.
5. Klykov, V.N. Sintez prirodnykh 3-O-(1-alkenil)kholesterinov [Synthesis of natural 3-O-(1-alkenyl)cholesterols] / V.N. Klykov, I. Yu. Mikhailova, G.A. Serebrennikova, R.G. Evstigneeva // Bioorganicheskaya Khimiya [Bioorganic Chemistry]. - 1979. – V.5. – P. 918–922. [in Russian]
6. Hu, X. Reaction pathways of glucose during esterification: effect of reaction parameters on the formation of humin type polymers / X. Hu, C. Lievens, A. Larcher, C.-Z. Li // Biores. Technol. – 2011. – Vol. 102. – P. 10104–10113.
7. Liu, J. Conversion of fructose into 5-hydroxymethylfurfural (HMF) and its derivatives promoted by inorganic salts in alcohol / J. Liu, Y. Tang, K. Wu // Carbohydr. Res. – 2012. – Vol. 350. – P. 20–24.
8. Nolic, G. Deconvoluted Fourier-transform LNT-IR study of coordination copper (II) compounds with dextran derivatives / G. Nolic, M. Cakic, Z. Mitic, L. Ilic // Rus. J. Coord. Chem. – 2008. – Vol. 34 – P. 322–328.
9. Formation, molecular structure, and morphology of numins in biomass conversion: influence of feedstock and processing condition / I. van Zandvoort, Y. Wang, C. Rasrendra et al // ChemSusChem. – 2013. – Vol. 6. – P. 1745–1758.