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SIDE REACTIONS OF ACID HYDROLYSIS OF SUCROSE

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Key words: sucrose, fructosylglucose, acid sucrose hydrolysis.

By-products formation during hydrolysis of sucrose was investigated. Formation of fructosylglucose at initial stage of hydrolysis as well as in the course of direct reaction of fructose and glucose was established. It was observed that condensation of fructose is the predominant side reaction of sucrose hydrolysis.

Hydrolysis of sucrose in dilute solutions is a monomolecular reaction [10, 14] following the mechanism of nucleophilic substitution S_N1 [4, 6, 10]. It is commonly known that because of kinetic reasons an invert obtained under mild conditions of hydrolysis from dilute sucrose solutions is virtually an equimolar mixture of fructose and glucose. This fact finds application in analytical procedures [1].

In condensed solutions of sucrose hydrolysis takes place along with numerous side reactions resulting from interaction between substrates and reaction products [27]. It was proved experimentally that prolonged boiling of a sucrose solution (65° Bx; pH = 6.2 or 3.5) leads not only to sucrose hydrolysis but also to formation of trisaccharides of kestose type and disaccharides, mainly difructosides [2]. The mechanism of kestose formation has not been quite clear as yet [2]. The formation of difructosides can be accounted for by condensation of fructose according to S_N2 mechanism [2, 4]. In acidic environment fructose undergoes condensation to three reducing difructosides, which are accompanied by fructose anhydrides, depending on reaction conditions [7, 13].

Considering fructose lability and its tendency to dissociation [8] it may be anticipated that the quality and quantity composition of the invert depends on reaction conditions. Presence of by-products in inverted technological sugar, used as a sweetener and a calorificc substance, is of no major significance. For example, the calorific value and sweetness of one of the products of fructose condensation, inubiolose, approximate analogous properties of sucrose [11].

Importance of the quantitative and qualitative compositions of the invert obtained from condensed solutions of saccharose may come to the fore when crystalline fructose and glucose are to be separated from products of sucrose hydrolysis. In such a case the bonding of fructose after sucrose hydrolysis in the form of difructosides reduces the quantity of fructose rendering itself to separation from the reaction mixture. Moreover, products of side reactions can have a negative influence on crystallization of fructose and glucose from the invert.

It follows from the above considerations that the tracing of formation of side reaction products during sucrose hydrolysis under the conditions of limited decomposition of fructose is a significant task. The present paper forms a continuation of earlier studies and it refers to the results of the analyses concerning fructose condensation in analogous circumstances [7]. For this reason it was interesting to compare the composition of sucrose hydrolysis products with the composition of fructose condensation as well as with the composition of products resulting from molecule interaction within the equi-molar mixture of fructose and glucose. The composition of such a mixture consists for an invert model.

THE EXPERIMENT

The sucrose hydrolysis was carried out using a sucrose solution concentrated at 0.62 g/cm^3.; pH = 1.3; temp. $-60° \pm 1°C$; time — 180 minutes. Solutions of fructose, glucose and equimolecular mixture of fructose and glucose were kept under the same conditions, their condensation parameters being equal with the above. Besides, two solutions of sucrose were subjected to hydrolysis under similar conditions. One of the solutions was more dilute and the other more condensed than the fundamental one.

After 30,50,60,100,120 and 180 minutes of sucrose hydrolysis samples were collected and analyzed as to optical rotation of the solution. The qualitative and quantitative composition of hydrolysis products was determined with paper chromatography. Whatman paper and a combination of solvents: propanol: ethyl acetate: water (7:1:2) was used for developing. Developing time: 48 or 72 hours.

The chromatograms were developed with resorcine and aniline reagents [9]. Quantitative determinations in eluates were based on the use of Roe's reagent [12]. The measurements of the optical rotation of the solution were used to determine the constant speed of the hydrolytic reaction and tthe degree of hydrolysis accomplished after a given period of reaction time.

RESULTS AND DISCUSSION

A CHROMATOGRAPHIC ANALYSIS OF SUCROSE HYDROLYSIS PRODUCTS AS CAMPARED WITH PRODUCTS OF FRUCTOSE CONDENSATION

During the preliminary experimentation period it became clear that a solution of glucose alone in the applied conditions did not show any change in composition in the chromatogram. This is so because glucose undergoes condensation under more drastic conditions than those sufficient for sucrose [6].

Significant qualitative differences, however, are observed in the composition of solutions heated for 50 minutes: fructose, equimolecular mixture of fructose and glucose, and sucrose. The composition of the solutions is illustrated in Photo No. 1. In order to identify the components not only the three solutions (samples 1, 2, 3) were imposed but also the standard solutions (samples 4 through 7) corresponding, respectively, to fructopiranosylfructose, difructose dianhydride, the mixture of sucrose and raffinose, and fructosylglucose, were added.

The distribution of chromatographic spots and the results of previous studies upon fructose condensation in acid solutions [7] make it possible to determine that the main products of fructose condensation in a mono--component solution are the following: fructopiranosylfructose (the spot located closest to the starting line in sample 1), and next come inulobiose and levanobiose, the latter being accompanied by difructose anhydride.

Products of intermolecular interaction of the equi-molecular mixture of fructose and glucose (sample 2, photo 1) are: fructosylglucose, fructopiranosylfructose and inulobiose. Fructosylglucose, which is closest to the starting line is sample 2, differs from other fructosides in the mixture by reacting with the aniline reagent and this is so because it is an aldose. Fructosylglucose is known as a product of transglycosilation [3].

Under the given reaction conditions (sample 3, Photo 1) sucrose undergoes partial hydrolysis with a simultaneous formation of fructopiranosylfructose, fructosylglucose and traces of trisaccharides (kestozes).

It transpires from the chromatogram in Photo 1 that the three analyzed solutions differ also in terms of the quantitative composition. Consequently, in the next stage of the investigations the quantitative analysis of composition of the three solutions was carried out. Samples for chromatography were collected after 30 minutes of hydrolysis time when sucrose was about 50% decomposed into its component sugars. The composition of products from side reactions is illustrated in the chromatogram given in Photo 2. Relative concentration of particular by-products determined with Roe's method is presented in Table 1. In the applied chromatographic arrangement inulobiose and sucrose cannot be separated because they have the same R_F value. Concentration of inulobiose in the investigated solution was calculated with an assumption that in the course of sucrose hydrolysis the ratio of inulobiose and fructopiranosylfructose concentrations is constant. In the completely inverted solutions the ratio is 1:2.

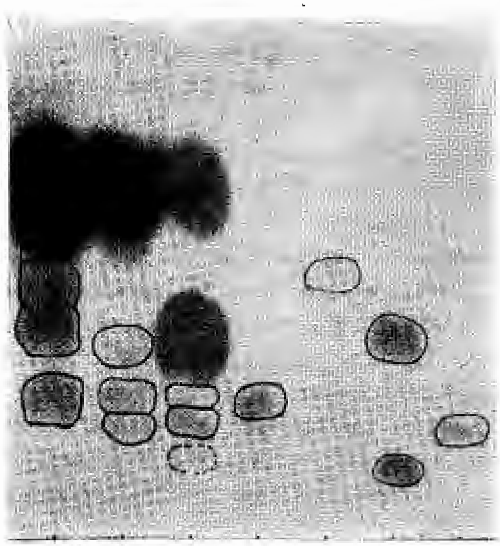

Fig. 1. Chromatogram of solutions: 1 — fructose, 2 — mixture of fructose and glucose, 3 — sucrose acidified with hydrochloric acid at pH 1.3 and kept at the temperature of 60°C during 50 minutes; reference samples: 4 — fructopiranosylfructose, 5 — difructose dianhydride, 6 — mixture of sucrose and rafinose, 7 — fructosylglucose

Table. Relative concentrations of individual reaction by--products after 30 min heating at 60°C of solutions: fructose (F), mixture of fructose and glucose (F+G) and sucrose (S). Solutions were acidified with hydrochloric acid at pH 1.3 Reference: concentration of inulobiose from mixture of fructose and glucose

Component	F	F+G	S
Difructose dianhydride	6	—	—
Inulobiose	8	1	0.3*)
Fructopiranosylfructose	10	0.9	0.5
Fructosylglucose	—	0.8	1.8
Trisaccharides (kestoses)	—	—	1.0
Total concentration of side reaction products	24	2.7	3.6
Total concentration in ratio of the F+G mixture	8.9	1.0	1.3

*) Estimated concentration

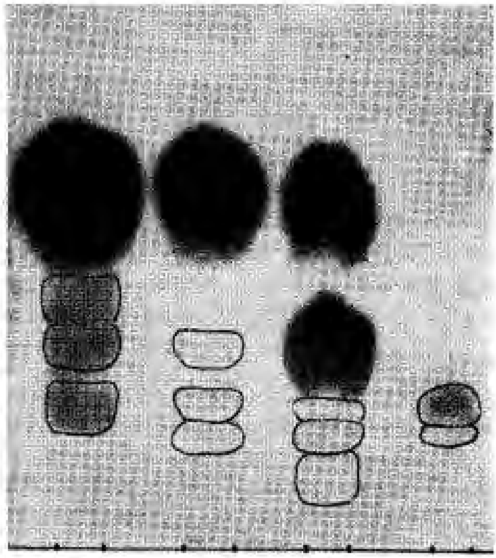

Fig. 2. Chromatogram of solutions just as on Fig. 1 after 30 minutes of reaction

It follows from the presented data that concentrations of byproducts formed in a pure fructose solution is almost nine times higher than in the case of the invert model, that is, the equimolecular mixture of fructose and glucose. If we assume that the process of fructose condensation in an acid solution follows the S_N2 mechanism then a double reduction of concentration of fructose in ratio of water should cause a four-fold reduction in the quantity of condensation products. However, the concentration of condensation products continues to be only two times smaller. This is due to the inhibiting effect of glucose on fructose condensation. Conspicuously perceivable is the absence of fructose anhydrides of fructose in the invert model solution.

In the sucrose solution hydrolyzed in half the concentration of by-products is 30% higher than in the model mixture. Fructosylglucose accounts at this stage of hydrolysis for 50% of all by-products. This fact indicates that α-D-glucopiranose bonded in sucrose or released during hydrolysis is more vulnerable to fructose than glucose is in the model invert. A wide band corresponding to trisaccharides points to occurrence of mixture of several components (kestoses). Totally they consist for 30% of by-products at that stage of hydrolysis. A relatively lower concentration of fructopiranosylfructose in the solution of hydrolyzed sucrose than in the model mixture is an evidence of the state of balance of fructose isomers effect on formation of by-products.

ANALYSES OF CHANGES OR THE SUCROSE HYDROLYSIS SIDE-REACTION PRODUCT COMPOSITION IN RELATION TO INVERSION TIME

Chromatogram No. 3 illustrates changes in the solution of hydrolyzed sucrose depending on reaction times: 30, 60, 100 and 120 min. It follows from the positioning and intensity of colours that prolongation of the hydrolytic reaction time from 30 to 60 minutes the concentration of disaccharides increases and concentration of trisaccharides decreases. After 60 minutes of reacting, when the degree of inversion is 0.9 the spots mixture (its R_F corresponds to fructose dianhydride) come in sight. After 100 and 120 minutes of reaction, when the inversion degree is 0.97 and above 0.99, the concentration of products of side reactions does not alter significantly. The mixture reaches the state of equilibrium. After full hydrolysis of sucrose the solution contains glucose, fructose, fructosylglucose, fructopiranosyfructose, inubiolose and traces of fructose anhydrides. Thus the by-products are dominated by products of fructose condensation. Consequently, total concentration of by-products depends on the initial concentration of sucrose, similarly as in the case of fructose [7]. This dependence is illustrated in Chromatogram No. 4. It was made with samples of three sucrose solutions with growing concentrations after 180 minutes; the inversion degree was 0.999.

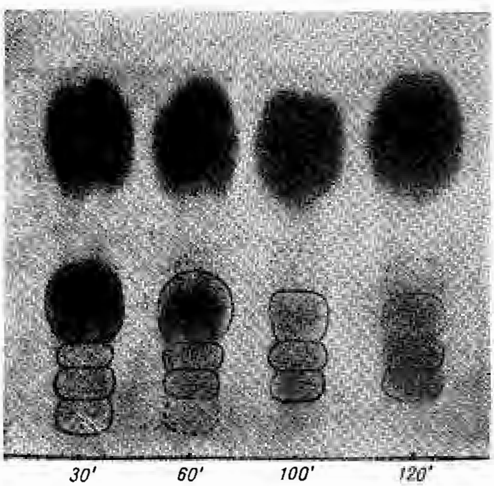

Fig. 3. Chromatogram of solutions of sucrose acidified with hydrochloric acid at pH 1.3 and kept at the temperature of 60°C during 30, 60, 120 minutes

In conclusion it can be said that sucrose hydrolysis in a concentrated solution in a moderate temperature (60°C) is accompanied by side reactions leading to formation of trisaccharides, fructose condensation products and fructosylglucose. Trisaccharides disappear in the solution at 0.9 inversion degree. Unexpectedly high presence of fructosylglucose in sucrose hydrolysis by-products was observed at the initial stage of hydrolyzing. The intermolecular condensation of fructose takes place simultane-

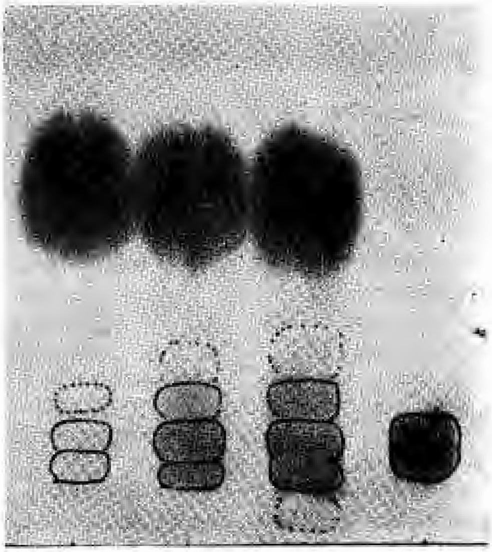

Fig. 4. Chromatogram of inwert sugar obtained from sucrose solutions, whose concentrations were arranged in the following increasing order 1, 2, 3; 4 — spot reference sample of fructosylfructose

ously with sucrose hydrolysis but also it gains in strength towards the end of hydrolyzing when fructose has been accumulated in the solution. Glucose impedes the condensation reactions of fructose. Total concentration of sucrose hydrolysis by-products increases with the growth of the initial concentration of the solution subjected to hydrolysis.

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REAKCJE UBOCZNE KWASOWEJ HYDROLIZY SACHAROZY

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STRESZCZENIE

Badano przebieg reakcji ubocznych hydrolizy sacharozy w temperaturze 60°C, w pH roztworu 1,3 i początkowym stężeniu sacharozy 0,62 g/cm^3.

Skład roztworów po hydrolizie porównano metodą chromatografii bibułowej ze składem modelowym roztworów czystej fruktozy i równomolowej mieszaniny fruktozy i glukozy utrzymywanych w warunkach analogicznych jak sacharoza.

Stwierdzono, że hydrolizie sacharozy towarzyszą reakcje uboczne, które prowadzą do powstawania trójsacharydów i dwusacharydów. Trójsacharydy zanikają całkowicie, gdy stopień inwersji wynosi ponad 0,9.

Dwusacharydy powstają w wyniku międzycząsteczkowej kondensacji fruktozy oraz w wyniku bezpośredniego oddziaływania fruktozy i glukozy. W całkowicie zhydrolizowanym roztworze sacharozy, obok glukozy i fruktozy, znajdują się dwucukry powstałe w wyniku kondensacji fruktozy oraz fruktozyglukoza. Sumaryczne stężenie produktów ubocznych zależy od początkowego stężenia roztworu sacharozy, podobnie jak to ma miejsce w przypadku fruktozy.