

## STUDY OF THE DEHYDRATION OF AN AQUEOUS SOLUTION OF MALTOTRIOSE BY THE IR-FOURIER SPECTROSCOPY

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### ABSTRACT

*In this paper, the changes in IR-Fourier spectra of aqueous maltotriose solution taking place during its dehydration have been analyzed. It is established that in the solution there is a reciprocal effect of the components at the level of the chemical bonds and molecules, the value of which depends on the water/carbohydrate ratio. As compared with maltotriose, the dehydration product of its solution contains more tightly bound water, which possibly "stitches" individual molecules of trisaccharide by binding to their  $\alpha$ -glycoside bridges. Individual oligosaccharides with a number of pyranose cycles in the molecules 3 - 7 behave like maltotriose.*

*Keywords: IR-Fourier spectrum, carbohydrate, saccharide, trisaccharide, maltotriose, dehydration.*

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### INTRODUCTION

The concept of carbohydrates has penetrated deeply into the life and human activity, as carbohydrates are a part of a variety of products, such as adhesives, glues, medical and pharmaceutical preparations. Trisaccharide molecules consist of three monosaccharide residues linked together by the interaction of hydroxyl groups. The general formula for trisaccharides is generally  $C_{18}H_{36}O_{18}$ . Trisaccharides can differ from one to another in the structure of their monosaccharides and their sequence in the chain, the size of the cycles (five-membered furanose or six-membered pyranose), the configuration of glycosidic centers and glycosyl residues to the aglycons. This causes tens of thousands of possible trisaccharide isomers. The monosaccharides also include raffinose, consisting of residues of D-galactose, D-glucose and D-fructose; melicitose, which consists of two residues of D-glucose and one residue of D-fructose. Maltotriose is also one of the known trisaccharides, consists of three residues of D-glucose [1, 2].

Of particular interest are solutions of carbohydrates in water, since it is in this form that many of the saccharides are used for their intended purpose or as precursors (raw materials, semi-products) in the preparation of products from them. The structure of aqueous solutions of carbohydrates is devoted to a significant number of spectroscopic studies, most of which consider substances with a simple molecular structure, for example, mono- and disaccharides [3 - 5], or, conversely, highly polymerized starches and dextrans [6 - 9]. There have also been published papers on the nature of intermediate forms of carbohydrates [10 - 13], but they almost did not touch upon the relationship of properties with the degree of polymerization of substances.

The aim of the work was to analyze the changes in the IR-Fourier spectra of an aqueous solution of maltotriose occurring during its dehydration. In this paper, using the method of IR Fourier spectroscopy, has been considered the dehydration of an aqueous solution of maltotriose, the molecule of which is constructed from identical pyranose rings connected by the same  $\alpha$ -glycosidic chemical bonds.

## EXPERIMENTAL

Dehydration of carbohydrate solutions was studied using the method of IR-Fourier's spectrometry in the regime of impaired total internal reflection (ITIR), and the products formed in this case were investigated using the method of thermal analysis. The IR spectra were recorded on a FT-IR Nicolet 6700 spectrometer from Thermo Electron Corporation at room temperature, with a resolution of  $4\text{ cm}^{-1}$ , an accuracy of  $\pm 0.5\text{ cm}^{-1}$ , and a scan number of 32.

An ITIR prefix with a ZnSe single crystal ( $45^\circ$ ) was used, which made it possible to record the spectra at a 12-fold reflection of an infrared laser beam with a beam penetration depth of about  $2\text{ }\mu\text{m}$  into the sample. The solution was applied in a thin layer on the surface of the single crystal, so that the contact area of the liquid with the solid surface was maximal. As the solution dried out, the spectra were recorded at intervals of about 0.5 hours.

Thermal analysis was performed on a combined thermal analysis instrument STA-449 F1 Jupiter from Netzsch. Samples weighing 3 - 4 mg. in the form of pieces of film formed during the drying of aqueous solutions in air at room temperature were heated in open alumina crucibles with a volume of  $85\text{ }\mu\text{l}$  at a speed of 5 degrees/min in a dry nitrogen atmosphere.

There were used commercial carbohydrates supplied by Sigma-Aldrich: maltotriose No. M8378, lot 017K0679; maltose No.M5885; maltotetraoz No.M8253, lot 109K1271; maltopentaose No.M8128, Lot 040M1774; maltohexaose No.M9153; maltoheptaose No.M7753, Lot 079K0987. Solutions of saccharides in distilled water with a concentration of about 10 % were prepared at room temperature.

## RESULTS AND DISCUSSION

The infrared spectrum of a solution of maltotriose differs very little from the same spectrum of water (Fig. 1). Only in the low-frequency region, where the saccharides show the strongest spectral lines related to the stretching (valence) vibrations of the chemical bonds C-O and C-C [14 - 16], weak absorption is observed. In the high-frequency region of the spectrum, where the stretching vibrations of OH bonds in  $\nu(\text{OH})$  water molecules are recorded, there are also slight differences, manifested in the mismatch of the line profile for the solution and for pure water, as well as  $17 - 20\text{ cm}^{-1}$  wider at half-height at the strip of solution. In addition, the peak of deformation oscillations  $\delta(\text{OH})$  in OH bonds in water

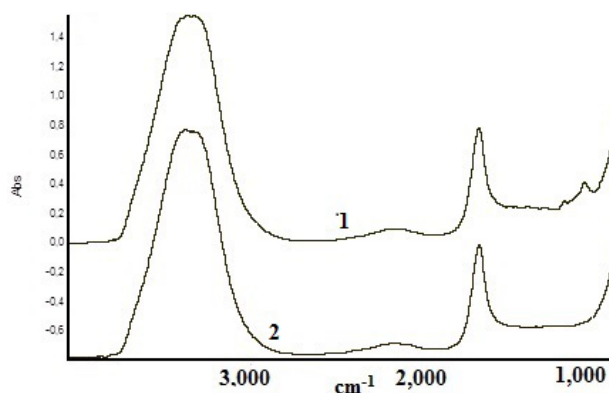


Fig. 1. IR-Fourier spectra of an aqueous solution of maltotriose (1) and water (2).

molecules (range  $1,560 - 1,800\text{ cm}^{-1}$ ) for the solution is slightly shifted to the high-frequency region. These differences, although not significant, are quite distinct and reproducible, and they indicate the effect of saccharide on water at the molecular level, as already reported, for example, in [17, 18].

As the maltotriose solution dries out due to an increase in its concentration, the spectral lines related to the stretching vibrations of the C-O and C-C chemical bonds become more pronounced, and the water bands, on the contrary, gradually weaken. Therefore, the ratio of their intensities can serve as a measure of the depth of dehydration for a saccharide solution.

From Fig. 2, it can be seen that the relation  $I_{\nu(\text{CO}+\text{CC})}/I_{\nu(\text{OH})}$  is initially small, since the sample is enriched with water, it increases slightly with time, and after two hours of drying it increases stepwise. After 3 - 3.5 hours

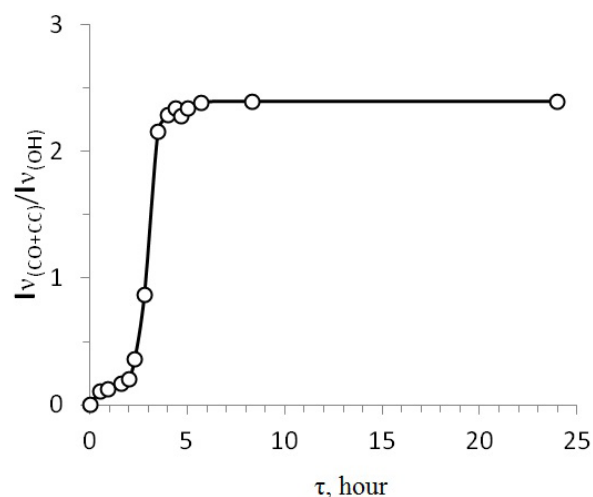


Fig. 2. Relative intensity of the  $\nu(\text{CO} + \text{CC})$  and  $\nu(\text{OH})$  lines in the IR spectra: dehydration products of an aqueous solution of maltotriose and reactive maltotriose.

it reaches the highest value and then almost does not change for a long time, remaining, however, significantly lower than in the spectrum of reactive maltotriose. There is only one explanation for this: the product of dehydration includes excess moisture, which is fairly strongly retained in the structure of the formed substance.

During the dehydration of the solution, not only the intensity of individual bands in the spectra changes, but also their nature. Thus, the most high-frequency of the  $\nu(\text{OH})$  bands, changing little in the initial stages of drying, after 3 - 3.5 hours of aging, narrows rather quickly, Fig. 3(a).

At the same time, its profile changes: the flattened top, which is typical for water, is replaced by a single maximum with an almost Gaussian character. The moment of the beginning of the transformation of the top of the line coincides with the appearance of absorption on its slope facing low frequencies, which refers to a complex of symmetric and asymmetric vibrations of C-H bonds in a saccharide molecule [3 - 6]. Such a transformation is also manifested at the maximum  $\delta(\text{OH})$ , which also increases its frequency stepwise, Fig. 3(b).

Changes in the spectra are even more significant in the region of stretching vibrations of the chemical bonds C-O and C-C. In Fig. 3(c) it can be seen that the profile of the dominant maxima is almost the same before the start of the above-mentioned transformation, and when it begins, it changes greatly with the frequency of the maximum. It should be noted that in this case, the strongest changes in the lines in the spectra of dehydration products coincide with the end of the jump in Fig. 2. Based on this, it can be stated that as the sample is dehydrated, the state of not only water but also saccharide molecules changes, that is there is a mutual effect of the solvent and the solute. And, judging by the nature of the IR spectra, the magnitude of this effect depends on the water/saccharide ratio.

The graphical analysis showed that the dominant maxima in the IR spectra of maltotriose and the product formed as a result of the drying of its aqueous solution are structurally different, although they consist of almost the same number of components, (Fig. 4). Thus, the lowest-frequency component from the spectrum of maltotriose turns out to be noticeably larger in the spectrum of the dehydration product, and the frequency following it, on the contrary, weakens. This confirms that maltotriose and the substance that formed from its

aqueous solution as a result of drying are not identical substances. The differences are indicated by the results of the study of both substances using the method of thermal analysis. According to them, the residual water begins to leave the product of dehydration no sooner than reactive maltotriose, as might be expected, but  $\sim 30^\circ\text{C}$  later, (Fig. 5). The loss of moisture when heated with

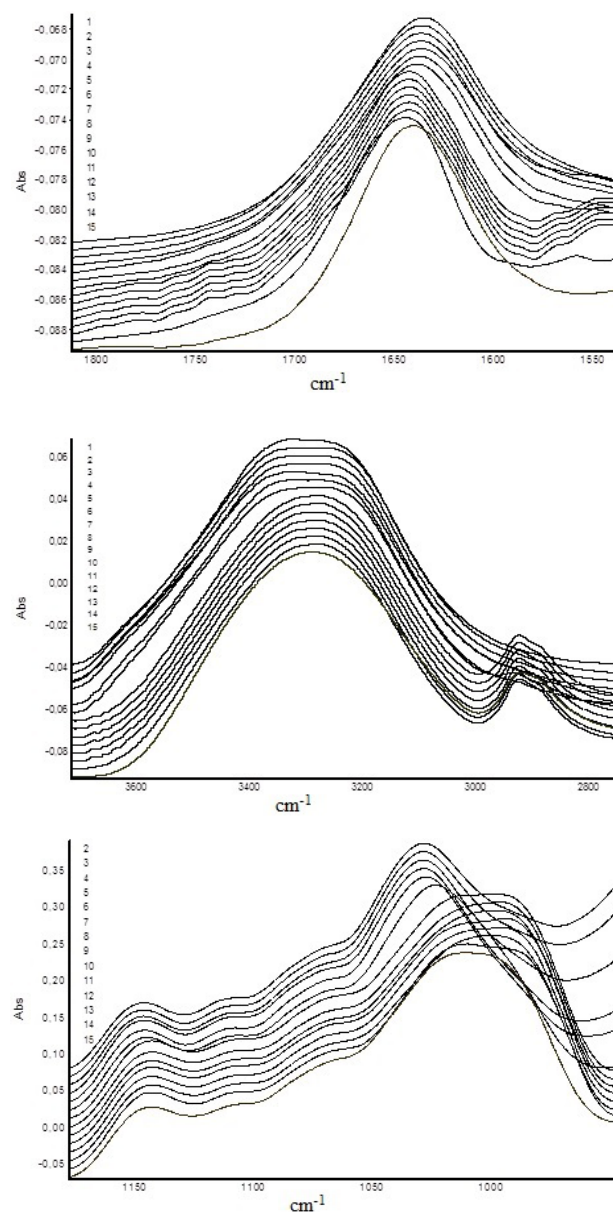


Fig. 3. High- and low-frequency regions (a-c) of the IR-Fourier spectra of water (1), an aqueous solution of maltotriose with a holding time, hour: 0.5 (2), 1.0 (3), 1.5 (4), 2.0 (5), 2.3 (6), 3.0 (7), 3.5 (8), 4.0 (9), 4.3 (10), 4.7 (11), 5.0 (12), 6.0 (13), 24 (14) and maltotriose (15). Spectra are numbered from top to bottom.

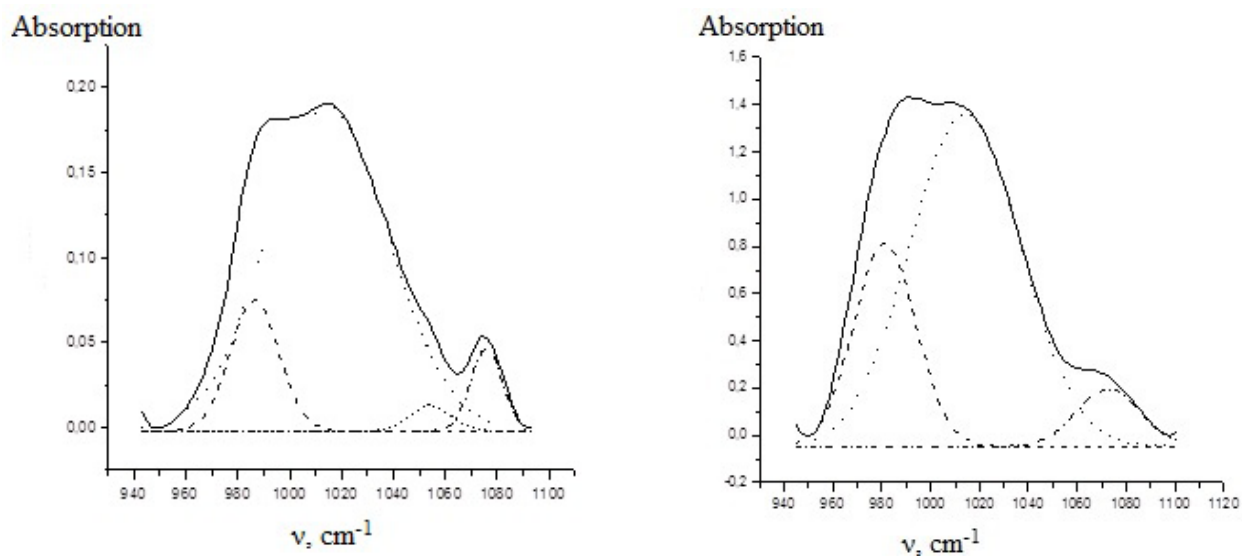


Fig. 4. The structure of the dominant maxima in the IR spectra of maltotriose (a) and the product of the dehydration of its aqueous solution (b).

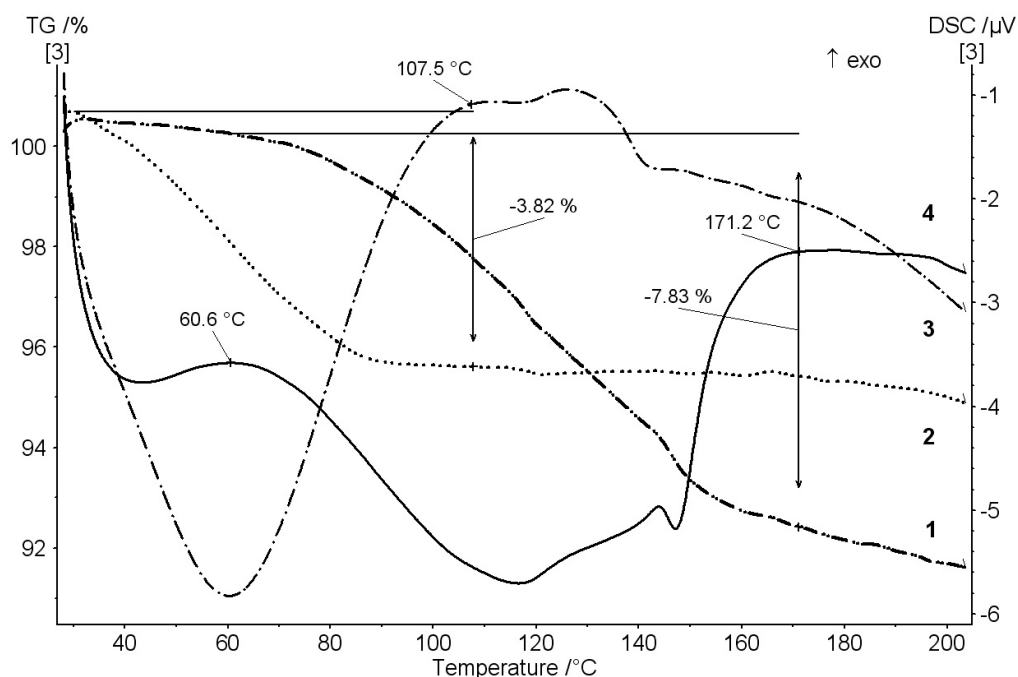


Fig. 5. Curves: TG of maltose (1) and the product of the dehydration of its aqueous solution (2), DSC of maltose (3) and the product of dehydration (4).

a trisaccharide ceases at about 107°C, and the process of dehydration product continues to 170°C - 200°C. In addition, the weight of the maltotriose sample is reduced by 3.8 %, while the dehydration product becomes 7.8 % lighter. From this it follows that water is contained in two samples in different quantities and it is variously related to the saccharide. If, in the case of a reactive

trisaccharide, this can be adsorbed moisture, then in the product of the dehydration of its solution is water, which is possibly related to the structure of the carbohydrate.

Returning to the results of the graphical analysis of the IR spectra, we note that we have suggested that in the IR spectra of individual oligosaccharides, the low-frequency component in the dominant band shows

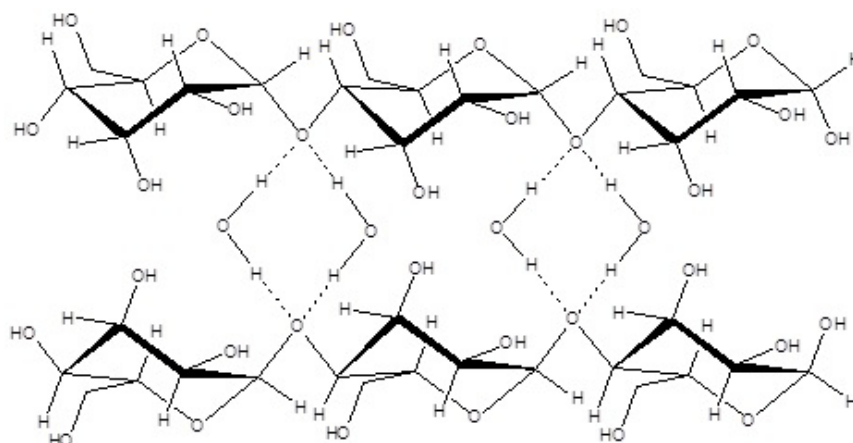


Fig. 6. The scheme of the dehydration of an aqueous solution of maltotriose offered on the base of IR-Fourier spectroscopy-research.

vibrations of  $\alpha$ -glycosidic bonds.

Therefore, a change in the magnitude of the corresponding calculated maximum in the spectrum of the dehydration product may be caused by changes in  $\alpha$ -glycosidic bridges under the influence of structurally related water molecules. The amount of the latter, found thermoanalytically by reducing the weight of the sample when heated, being related to the amount of carbohydrate in the sample, gives a molecular ratio of water/saccharide in the product close to two. This means that for each  $\alpha$ -glycosidic bridge there is one  $H_2O$  molecule. The most likely structure of dehydrated maltotriose can be represented by a scheme (Fig. 6) in which the water molecules bind simultaneously with two saccharide molecules, acting as a crosslinking agent.

Crosslinking can be one of the reasons for the high viscosity of the maltotriose that is not fully dehydrated and that water is retained in it after drying under room conditions.

Similar to maltotriose, when dehydrating aqueous solutions, other individual oligosaccharides behave with up to 7 pyranose cycles in molecules. The dynamics of the main lines in their IR spectra are almost the same, and the products of dehydration at room temperature also contain water and carbohydrate in a form different from the individual compounds.

## CONCLUSIONS

Thus, changes in the intensity, frequency and nature of the main peaks in the IR spectra of maltotriose aqueous solutions occurring during dehydration indicate a significant mutual effect of the components of the solutions at

the level of chemical bonds and molecules. Compared with reactive maltotriose, the product of the dehydration of an aqueous solution of this substance contains much more water, which, moreover, is more strongly associated with the trisaccharide. According to the results of the study, it can be assumed that water in the dehydration product is associated with  $\alpha$ -glycosidic bridges of the individual trisaccharide molecules, due to which cross-linking between them and the formation of viscous substances and films are ensured. Individual oligosaccharides with the number of pyranose cycles in molecules 4 - 7 with the dehydration of their aqueous solutions behave in the same way, which allows to extend the conclusions about the behavior of maltotriose and to them.

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