

# Water Adsorption Characteristics of Acyclic Oligosaccharides of $\alpha$ -Glucose Studied by Near Infrared Spectroscopy

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**Abstract:** The adsorption properties of water molecules on maltooligosaccharides are attributed to the OH groups of the glucose rings in maltooligosaccharides. The water molecules are adsorbed onto OH groups by hydrogen bond formation. Near infrared spectroscopic and gravimetric techniques were used in analysing the adsorption characteristics of maltooligosaccharides. Near infrared spectra of the dry maltooligosaccharides were acquired during the adsorption of water molecules at a relative humidity of 50%. The amounts of water adsorbed by the samples were also recorded by an analytical balance. Second derivative techniques were used in decomposing the OH combination frequency of the adsorbed water molecules in the region 5300-5000  $\text{cm}^{-1}$ .

The results indicate that the water molecules are adsorbed on to C2 and C3-OH groups at a higher rate compared to the adsorption onto C1-OH groups in the molecules. Adsorption also takes place onto the ethereal oxygen atoms in the glucose rings. The gravimetric results show that the adsorption of water molecules increases with the number of glucose units in the maltooligosaccharides except maltotriose which has the highest adsorption over a period of 75 minutes.

**Keywords:** Adsorption, Derivative profiles, near infrared, maltooligosaccharides,

## INTRODUCTION

Oligosaccharides are saccharide polymers containing simple sugar monomers. There are several different varieties of oligosaccharides containing different sugar monomers such as fructose, galactose, glucose etc. They are found in plants as free compounds and in the form of glycosides. Some plants house large amounts of oligosaccharides. For example, oligosaccharide raffinose is found in vegetables like cabbage, broccoli and asparagus. Fructo oligosaccharides are found in leeks and onions.

Maltooligosaccharides are polymers consisting of  $\alpha$ -glucose monomers that are found in partially hydrolysed starch and can contain from 1 to 12 glucose units [1]. The glucose units in these oligosaccharides are bonded by 1, 4-glycosidic bondings. Maltose, maltotriose, maltotetraose, maltopentaose, maltohexaose and maltoheptaose contain 2, 3, 4, 5, 6 and 7 glucose units respectively in them. The nature of the chemical bondings between  $\alpha$ -glucose units in the molecules gives the OH groups in them characteristic orientations in space.

Like carbohydrate polymers oligosaccharides have tendency to adsorb water molecules by forming hydrogen bonds with OH groups in the glucose rings. However, the mechanism of adsorption can be different. In carbohydrate

polymers, the adsorption takes place at the solid/solid interface but in the oligosaccharides the adsorption takes place at the solid/vapour interface. Humectant properties of maltooligosaccharides have been studied in the past by several authors [1, 2]. These articles give general information on how the humectant properties vary between the members in the group. The humectant properties of the maltooligosaccharides are attributed to the primary and secondary OH groups in the molecules. However, the study of chemistry and the progress during the adsorption of water molecules by these compounds are rare in the literature.

Christy has published a series of articles related to the nature of OH groups in different substances and their affinity to water molecules [3-6]. The use of Near Infrared Spectroscopy (NIR) and derivative techniques of the Spectra gave insight into the chemistry of the progress of water molecular adsorption taking place in these systems. Differentiation between the OH groups on the surface of the adsorbent was made and the rate of adsorption of water molecules by these OH groups was followed. The NIR spectrum of an adsorbent containing OH group exhibits a unique peak in the region 5300-5000  $\text{cm}^{-1}$  when water molecules hydrogen bond to the OH groups on the adsorbent. The absorption arises due to the combination frequency of the water molecular OH stretching and bending vibrations. Since this peak arises purely from water molecules adsorbed on to the OH groups on the surface of the adsorbent, the band structure of the above peak revealed by the second and fourth derivative techniques can be directly connected to the different types of surface OH groups.

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The assignments of the bands to different OH groups in the carbohydrate polymers were achieved by comparison technique. A detailed description of this can be found in reference 6. A similar approach was used in studying the humectant properties of maltooligosaccharides containing 3-7 glucose units.

The intention in this article is to show the characteristics of the hydroxyl groups in oligosaccharides and their adsorption properties towards water molecules. This was achieved by analysing the evolution of the NIR spectra during the adsorption of water molecules. Furthermore, Gravimetric method was used in studying the bulk properties of the oligosaccharides. The characteristics of the OH groups in oligosaccharides were used in explaining the differences in gravimetric results.

## EXPERIMENTAL

### Samples and Procedures

Oligosaccharides maltose, maltotriose, maltotetraose, maltopentaose and maltoheptaose were purchased from Sigma-Aldrich. All the samples had purity over 95%. The samples were finely ground to achieve similar particle size distribution.

All the oligosaccharides were first dried at 120 °C using a ceramic heater (BA Electric Bunsen from Electro thermal, Staffordshire, U.K.). A powerful vacuum pump was used in evacuating the water adsorbed on the samples. A K-type thermocouple was used in measuring the temperature in the sample during heating. After the evacuation process, each sample was cooled and controlled for any adsorbed water molecules by measuring the NIR spectrum of the sample. The absence of a peak in the 5300-5000  $\text{cm}^{-1}$  region would confirm the total removal of the adsorbed water molecules.

The removal of pre-adsorbed water molecules is important in order to study the priority and rates of adsorption of water molecules by different OH groups in the oligosaccharides.

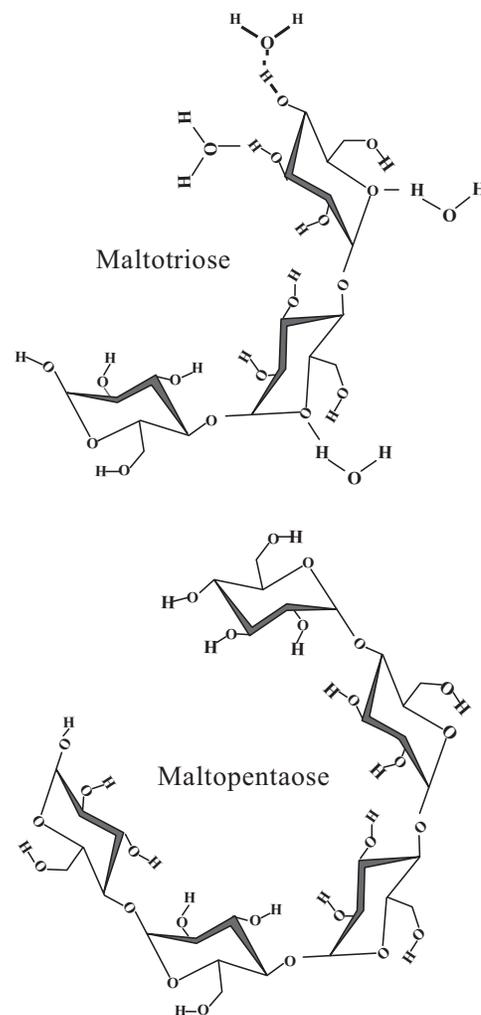
The water adsorption evolution of each sample was followed by gravimetry and NIR spectrometry. Adsorption of water molecules by a carbohydrate depends on the humidity of the surrounding and special setup was made to provide the same humidity to the sample surrounding during the gravimetric and NIR measurements. The relative humidities were controlled by a glycerol/water system [7]. The amount of glycerol was adjusted so that the relative humidity of the air in the surrounding of the samples during measurements was 50%.

The gravimetric determination of water sorption was carried out by quickly spreading 0,04g of an oligosaccharide sample in the NIR sample cup and placing it on a Mettler electronic balance that is capable of recording the weight increase of the sample up to 0.0001g. The balance was connected to a computer through a RS232 port and the data from the balance was recorded by communicating with the balance using locally made software. The increase in the mass of the sample was recorded twice each second. The data collected at the computer were imported into an Excel spread sheet and presented in the form of graphs for comparison and discussion.

The NIR measurements were made using a Perkin-Elmer Spectrum One NTS FT-NIR spectrometer (Perkin- Elmer Ltd., Cambridge, U.K.) equipped with a transreflectance accessory and deuterated triglycine sulphate detector. Around 0,04g of the dry oligosaccharide sample was quickly placed and spread in the NIR sample cup and moved on the ZnSe crystal of the transreflectance accessory that is covered by the chamber that provided an environment of air with 50% relative humidity. The spectral evolution was recorded frequently in the range of 10000–4000  $\text{cm}^{-1}$ . A total of 30 scans were obtained at a resolution of 16  $\text{cm}^{-1}$ . All the NIR spectra were transformed into log (1/R) format and second-derivative profiles of the spectral data were calculated by an algorithm developed by Savitzky and Golay with a 19-point derivative width. The fourth-derivative profiles of the spectra were obtained in the same manner from the second-derivative profiles.

## RESULTS AND DISCUSSION

The oligosaccharides used in the adsorption experiments in this article are compounds made up by  $\alpha$ -glucose units. The chemical structures of maltotriose and maltopentaose are



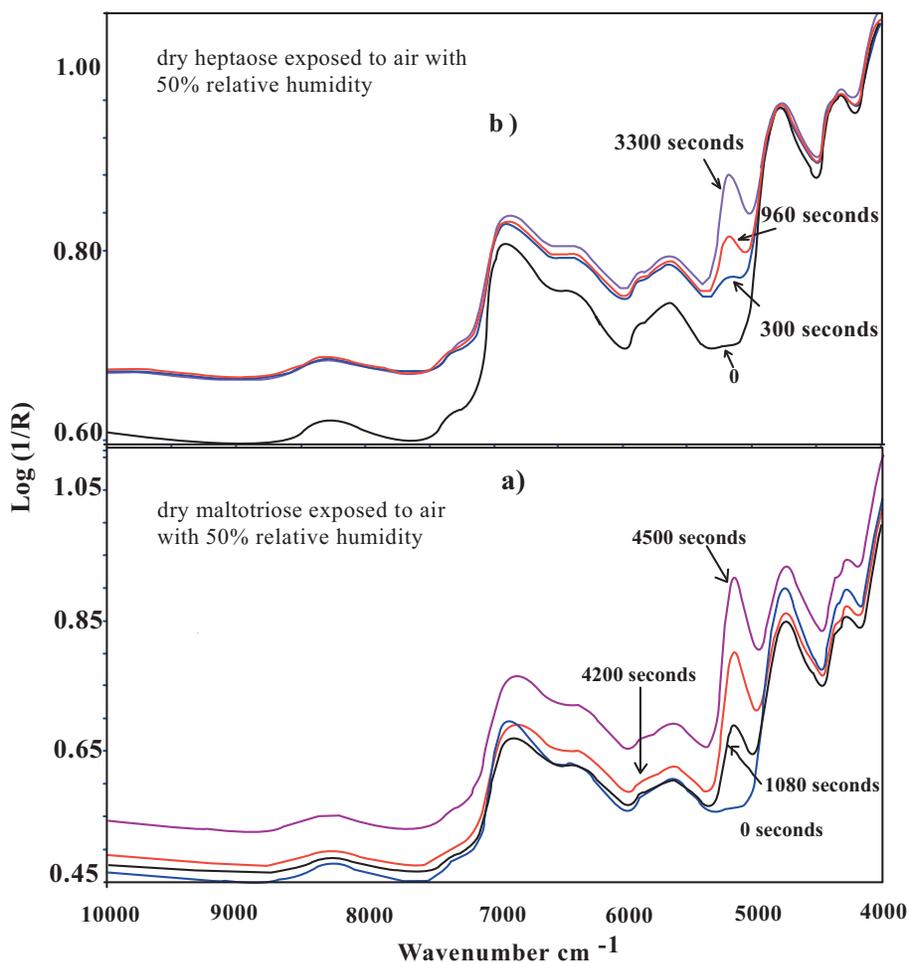
**Fig. (1).** Chemical structures of maltotriose and maltopentaose. The possible adsorption sites for water molecules is also shown for maltotriose.

shown in Fig. (1). Some possible interaction of water molecules with the OH groups on the maltotriose are also shown in Fig. (1). The NIR spectra of the dry maltotriose and maltoheptaose acquired during the adsorption of water molecules from the surroundings at a relative humidity of 50% are shown in Fig. (2). The spectra show the general features appearing in the NIR region. The characteristic NIR band assignments of the oligosaccharides with adsorbed water are similar to the carbohydrate polymers with adsorbed water and can be found elsewhere [6]. The putative NIR band assignments for the water molecules that are hydrogen bond-

ed to the OH groups of the glucose units in the oligosaccharide molecules can be found in Table 1. A striking observation that can easily be made in the NIR spectra is the absence of overtones of the free -OH (no sharp bands in the region  $7500\text{-}6000\text{ cm}^{-1}$ ) groups in the glucose units of the oligosaccharides. However, the second derivative profiles of the NIR spectrum of dry maltotriose (Fig. 3) reveals a broad peak containing the absorption bands of the hydrogen bonded OH groups in the samples. These absorptions were covered by the CH combination frequencies appearing in the neighbourhood.

**Table 1.** The NIR band Assignments for the Water Molecules Hydrogen Bonded to the OH Groups of the Carbohydrate Molecules

Band Position $\text{cm}^{-1}$	Assignment-Combination Frequency of the (OH Stretching and Bending Vibrations) of the Water Molecules Hydrogen Bonding to Groups in the Glucose Units
5246	OH groups at C2 and C3
5210	OH group at C4
5194	OH group at C6
5165	OH group at C1
5130	-O- ring O of the glucose units



**Fig. (2).** The NIR spectra acquired during the adsorption of water molecules at a relative humidity of 50% by a) maltotriose and b) maltoheptaose.

The NIR spectra in Fig. (2) show that the intensity of the absorption band arising from the combination frequencies of the water molecules increases in the samples. This is also the case with maltose, maltotetraose and maltopentaose. However, the rates of increase vary in the samples. Fourth derivative profiles of the NIR spectra acquired during the water adsorption evolution on maltotriose in the range 5300-5000  $\text{cm}^{-1}$  are shown in Fig. (4). The variations in the absorption peaks arising from the combination frequencies of the OH groups of water molecules hydrogen bonding to OH groups in the glucose units in the above oligosaccharides are clear. The water molecules adsorbed on to the OH groups of C2 and C3 give rise to an absorption band at 5246  $\text{cm}^{-1}$  [6]. The combined rate of adsorption of water molecules on the C2 and C3-OH groups has a higher rate compared to the C1-OH group. The behaviour is similar to the adsorption behaviour of C2 and C3 OH groups of carbohydrate polymers such as amylose, amylopectin and cellulose [6]. Absorption around

5130  $\text{cm}^{-1}$  is an indication that some water molecules form hydrogen bonding with ethereal oxygen (-O-) in the glucose rings.

The gravimetric adsorption results of the oligosaccharides are strange in terms of adsorption characteristics (Fig. 5). The maltose molecules have very low adsorption of water molecules. In contrast maltotriose has relatively high adsorption compared to all the other oligosaccharides. The fact that the maltose molecules engage in hydrogen bondings in crystalline state make the OH groups less available for hydrogen bonding with water molecules. The presence of inter and intra molecular hydrogen bondings in oligosaccharides such as glucose and maltose have been shown by nmr [8] and x-ray diffraction studies [9]. In maltotriose the addition of one glucose unit makes it difficult for inter hydrogen bonding with other maltotriose molecules [2] and the ring OH groups are available for hydrogen bonding with water molecules.

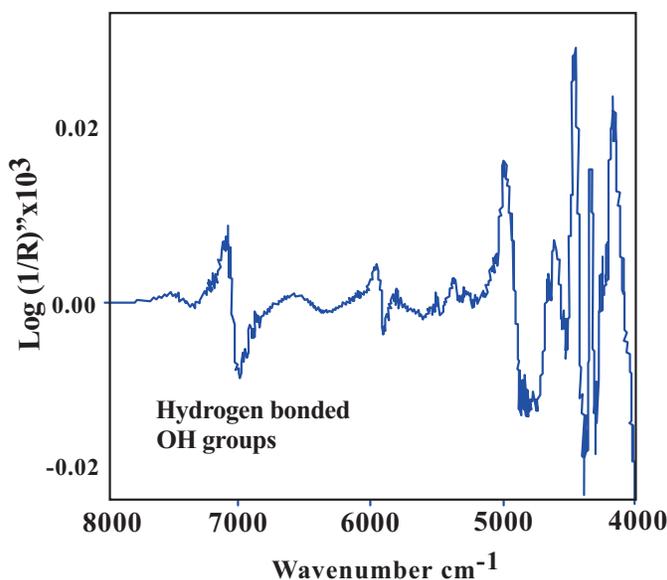


Fig. (3). Second derivative profiles  $[\text{Log}(1/R)']'$  of the NIR spectrum of dry maltotriose in the region 8000-4000  $\text{cm}^{-1}$ .

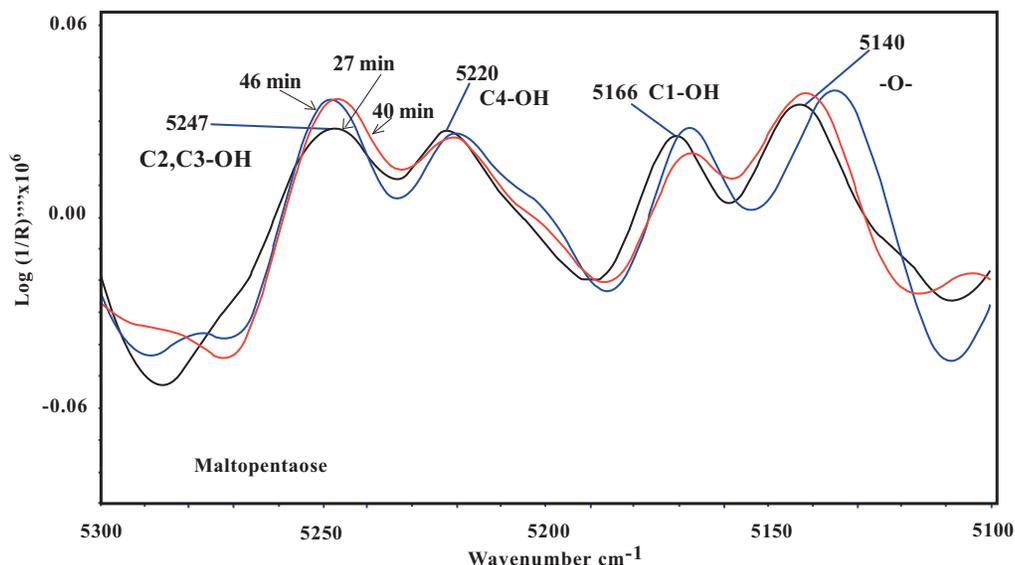


Fig. (4). The fourth derivative profiles of the NIR spectra acquired during the adsorption of water molecules by dry maltotriose sample.

Maltopentaose and maltoheptaose adsorb less water compared to maltotriose. Maltose and maltotetraose have similar adsorption curves.

The effect of heat on the oligosaccharides is illustrated by the adsorption behaviour of maltotetraose treated at two different temperatures. The adsorption curves are shown in Fig. (6). The effect of heat on the adsorption characteristics of maltotetraose is very clear. The mass of water adsorbed by maltotetraose heated at 180 °C was reduced to almost one fourth compared to maltotetraose treated at 120 °C. The heating dehydrates the sample. The OH group from one molecule condenses with OH group on another molecule. Similar result is shown for maltoheptaose in Fig. (7). The heating process eliminates the OH groups and therefore the

chances for the sample to engage in hydrogen bonding with water molecules are reduced. The sample also becomes yellow indicating the formation of bulky molecules.

## CONCLUSION

The adsorption characteristics of maltooligosaccharides containing 2 to 7 glucose units have been enlightened in this article. The characteristics are similar to carbohydrate polymers such as amylose and amylopectin. The OH groups attached to C2 and C3 adsorb water molecules at a higher rate compared to the primary OH group at C6. It is probably the OH group on C6 is in a less energetic position. There is also evidence that some water molecules adsorb onto the

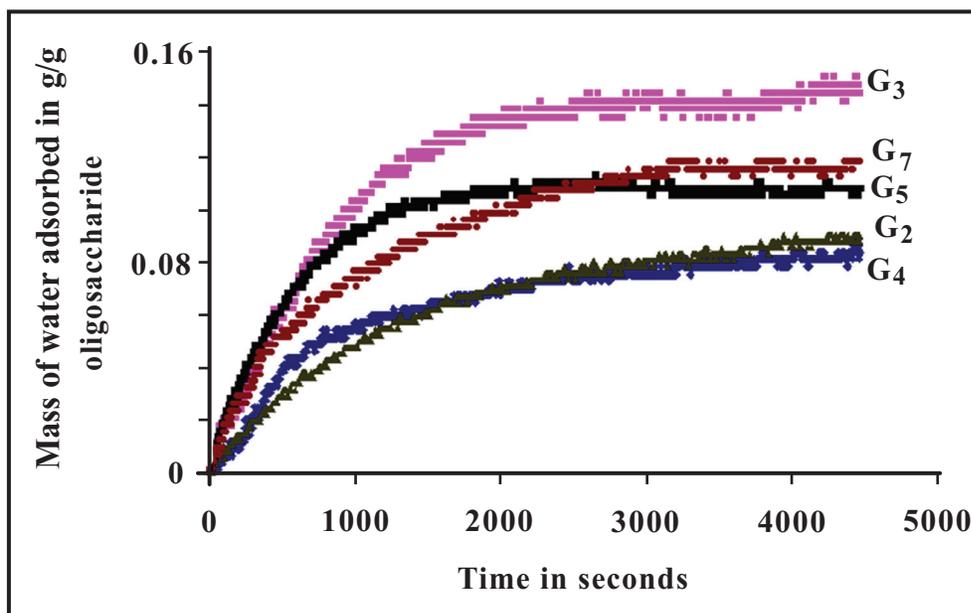


Fig. (5). A combined plots showing the Mass of water adsorbed by oligosaccharides during the first 4000 seconds. Plot for maltose (G2), maltotriose (G3), maltotetraose (G4), maltopentaose (G5) and maltoheptaose (G7)

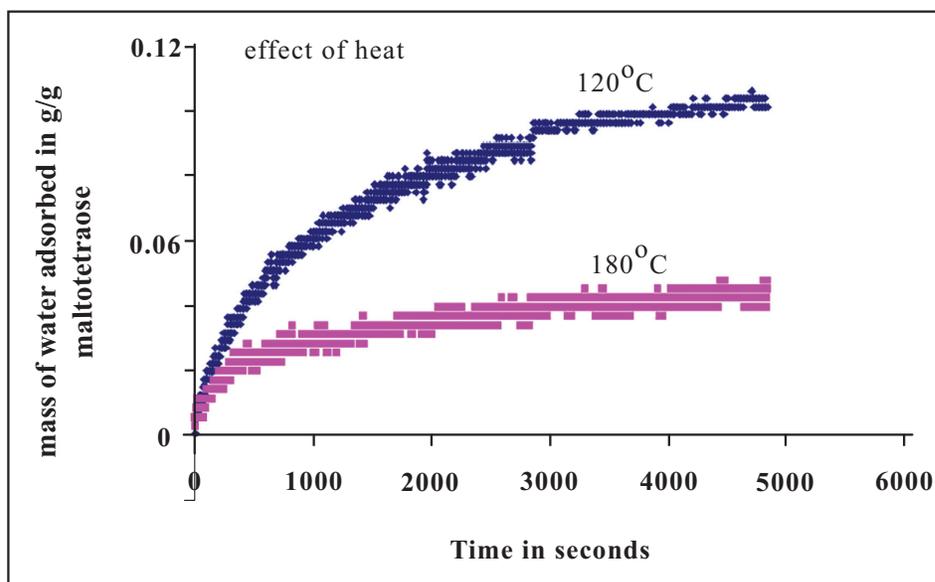
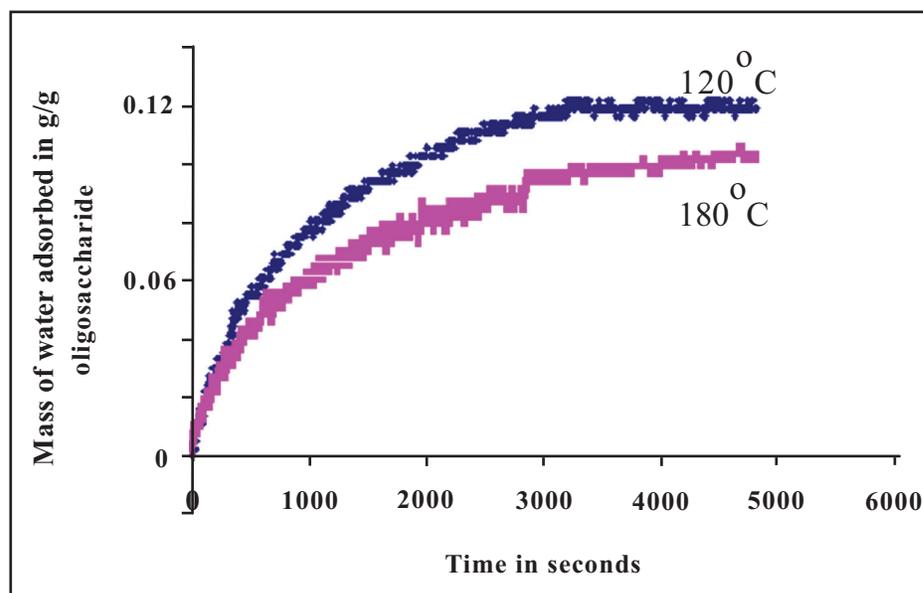


Fig. (6). The effect of heat on the water adsorption characteristics of maltotriose at temperatures 120 and 180 °C.



**Fig. (7).** The effect of heat on the water adsorption characteristics of maltotriose at temperatures 120 and 180 °C.

etheral oxygen of the glucose units.

The gravimetric results show that the maltotriose adsorbs more water than the oligosaccharides maltose, maltotetraose, maltopentaose and maltoheptaose at a relative humidity of 50%. This agrees with the results reported in the literature [1, 2]. Maltose adsorbs less water compared to all the other oligosaccharides used in this work.

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