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Thermal behaviour of anhydrous, dihydrate and (2/1) ethanol forms of 1-O-α-D-glucopyranosyl-D-mannitol

P. Perkkalainen, H. Halttunen, I. Pitkänen*

University of Jyväskylä, Department of Chemistry, P.O. Box 45, FIN-40351 Jyväskylä, Finland

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Abstract

The melting points of anhydrous 1-O-α-D-glucopyranosyl-D-mannitol, 1-O-α-D-glucopyranosyl-D-mannitol dihydrate and a new compound, 1-O-α-D-glucopyranosyl-D-mannitol-ethanol (2/1) were determined using differential scanning calorimetry. The melting onset values were 169.2 (3), 104.3 (18) and 158.7 (9), respectively, and the melting peak values were 171.4 (5), 107.9 (15) and 160.1 (6), respectively. 1-O-α-D-glucopyranosyl-D-mannitol dihydrate and 1-O-α-D-glucopyranosyl-D-mannitol-ethanol (2/1) decompose to anhydrous form when heated at slow heating rates.

According to TG-FTIR measurements, 1-O-α-D-glucopyranosyl-D-mannitol-ethanol (2/1) lost its ethanol in the 110–190°C range, and 1-O-α-D-glucopyranosyl-D-mannitol dihydrate lost its crystal water in the 60–210°C range. After removal of ethanol and crystal water, both decomposed in air totally as carbohydrates usually do, forming lower hydrocarbons with OH-groups, CO_2 and H_2O. © 1998 Elsevier Science B.V.

Keywords: 1-O-α-D-glucopyranosyl-D-mannitol; Glucopyranosylmannitol; Melting point; Thermal behaviour; Thermal decomposition

1. Introduction

The equimolar mixture of 1-O-α-D-glucopyranosyl-D-mannitol (synonyms glucopyranosylmannitol, GPM) and 6-O-α-D-glucopyranosyl-D-sorbitol (synonyms glucopyranosylsorbitol, GPS) is used as an artificial sweetener called isomalt [1]. The glucopyranosylmannitol part of isomalt crystallizes from aqueous solutions as dihydrate [2], while the glucopyranosylsorbitol part crystallizes in an anhydrous form [3]. Both are disaccharide alcohols consisting of a glucopyranosyl ring and a polyol side chain. The solution calorimetry measurements for isomalt and its components has been published, as well as the fusion and glass-transition temperatures for glucopyranosylsorbitol and anhydrous glucopyranosylmannitol [4]. Our interest was to determine the melting onsets and peaks for anhydrous glucopyranosylmannitol and glucopyranosylmannitol dihydrate and for a new compound, glucopyranosylmannitol-ethanol (2/1), and to examine the thermal decomposition of these compounds. The melting onset and peak values for an intermediate compound, glucopyranosylmannitol monohydrate, were also obtained from the DSC measurements of glucopyranosylmannitol dihydrate. The molecular formula of glucopyranosylmannitol is shown in Fig. 1.

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*Corresponding author. Tel.: +358-14-283786; fax: +358-14-602501; e-mail: perkkalainen@jykem.jyu.fi

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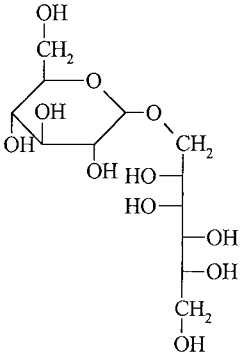

Fig. 1. The molecular formula of glucopyranosylmannitol.

2. Experimental

Pure (99.5% on a dry substance, determined by Varian 5500 HPLC equipped with strong acid cation exchanger and HP1047 RI-detector) 1-O-α-D-glucopyranosyl-D-mannitol dihydrate crystals were obtained from Cultor. Anhydrous 1-O-α-D-glucopyranosyl-D-mannitol was prepared by drying the dihydrate crystals in an oven at 80°C for two days. 1-O-α-D-Glucopyranosyl-D-mannitol-ethanol (2/1) was crystallized from aqueous ethanol solution at elevated temperatures. The structures of anhydrous glucopyranosylmannitol and glucopyranosylmannitol dihydrate were confirmed with X-ray powder diffraction measurements [5]. The crystal structure of 1-O-α-D-glucopyranosyl-D-mannitol-ethanol (2/1) was resolved with X-ray single crystal methods, and it will be published elsewhere.

The DSC measurements were carried out on Perkin–Elmer DSC-7 using 50 μl aluminium sample pans with holes and dynamic nitrogen atmosphere with a flow rate of 40–50 ml min^{-1}. The sample weights were 4–6 mg, the temperature range was 30–200°C and the heating rates were 25, 20, 15, 10, 5, 2 and 0.5°C min^{-1}. Two parallel measurements were made at a heating rate of 0.5°C min^{-1}, and six parallel measurements at other heating rates. Indium and benzoic acid were used for calibrating the temperature and indium was used for calibrating the enthalpy. The calibrations were carried out at the same heating rate as were the measurements.

The melting onsets and peaks were determined for each sample by linear regression using the average values obtained for six parallel measurements as data points. The program used was Origin^{TM} [6]. The melting points and onsets were determined by extrapolating the heating rate to an isothermal situation.

The TG-FTIR measurements were carried out on a Perkin–Elmer TGA 7 using open Pt-pans in dynamic air with a flow rate of 70–80 ml min^{-1}. The sample weights were 9–11 mg and the heating rate was 10°C min^{-1}. The volatile gases were analyzed with a Perkin–Elmer System 2000 FT-IR using a resolution of 8 cm^{-1}. The number of scans was 16. The FTIR data were collected using Perkin–Elmer TR-IR software. [7]

3. Results

3.1. DSC measurements

The melting peaks and onsets (with standard deviations in brackets) for anhydrous glucopyranosylmannitol, glucopyranosylmannitol dihydrate and glucopyranosylmannitol-ethanol (2/1) are presented in Table 1. The correlation coefficient is given as the *R*-value and S.D. is the standard deviation of the fit. The *P* value is the probability of *R* being zero. The high values of correlation coefficient and the small values of probability thus indicate a high correlation between the heating rate and the melting points. The small values of the standard deviation of the fit indicate the success of the linear regression and, thus, the good quality of the measured data.

The melting peak and onset values and the heating rate of anhydrous glucopyranosylmannitol have the highest correlation values and those of glucopyranosylmannitol dihydrate the lowest correlation values. The most accurate onset and peak values can be obtained for anhydrous glucopyranosylmannitol. This is well understood as the DSC-curves of the anhydrous glucopyranosylmannitol only have one melting endotherm, while the DSC-curves of glucopyranosylmannitol dihydrate and glucopyranosylmannitol-ethanol (2/1) are much more complex due to the monotropic polymorphism of these compounds. The DSC curve of glucopyranosylmannitol dihydrate measured with 2°C min^{-1} contains an endotherm caused by the partial evaporation of the crystal water followed by the melting peak of glucopyranosylmannitol dihydrate. Immediately after the melting endotherm, a

Table 1
The melting peaks and onsets for anhydrous glucopyranosylmannitol, glucopyranosylmannitol dihydrate and glucopyranosylmannitol-ethanol (2/1) using linear regression. The standard deviations of the peaks and the onsets are in parenthesis. *R*, correlation coefficient; SD, standard deviation of the fit, and *P*, the probability (that *R* is zero)

	Anhydrous glucopyranosylmannitol	Glucopyranosylmannitol dihydrate	Glucopyranosylmannitol-ethanol (2/1)
Onset/°C	169.2(3)	104.3(18)	158.7(9)
R	0.7845	0.3300	0.5892
S.D.	0.56	2.87	1.16
P	0.037	0.470	0.411
Peak/°C	171.4(5)	107.9(15)	160.1(6)
R	0.9004	0.5831	0.7994
S.D.	0.80	1.98	0.85
P	0.006	0.225	0.056

minor exotherm is noticed. Then, in the region of ca. 120–150°C many minor endotherms are noticed. These small peaks are caused by the evaporation of the residual crystal water and the melting of the intermediate compound, glucopyranosylmannitol monohydrate. The final peak, thus, is the melting peak of anhydrous glucopyranosylmannitol. With higher heating rates only three endothermic peaks can be noticed, namely the melting endotherm of glucopyranosylmannitol dihydrate mixed with evaporation endotherm of the crystal water molecules, the melting endotherm of anhydrous glucopyranosylmannitol and the melting peak of the intermediate compound, glucopyranosylmannitol monohydrate, at 120–150°C. Because the melting endotherm of glucopyranosylmannitol dihydrate and the evaporation endotherm of the crystal water are not resolved, a large deviation in the results of the melting point determination of

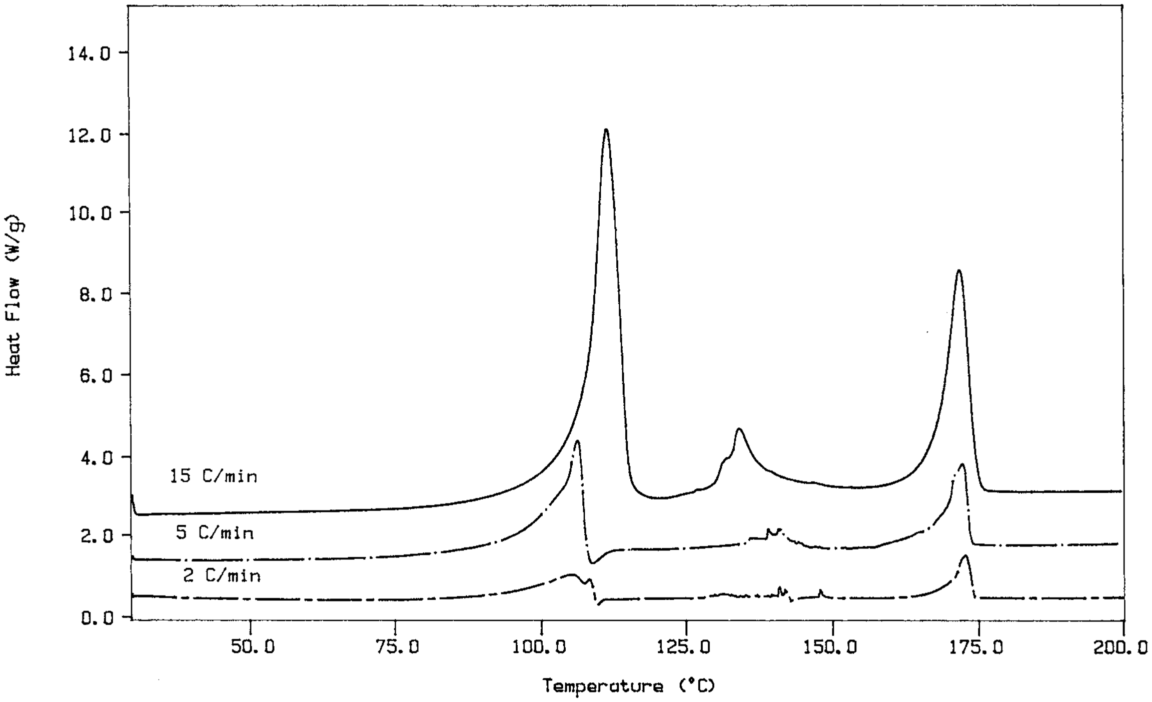

Fig. 2. The DSC curves for glucopyranosylmannitol dihydrate measured with heating rates 2, 5 and 15°C min^{-1}.

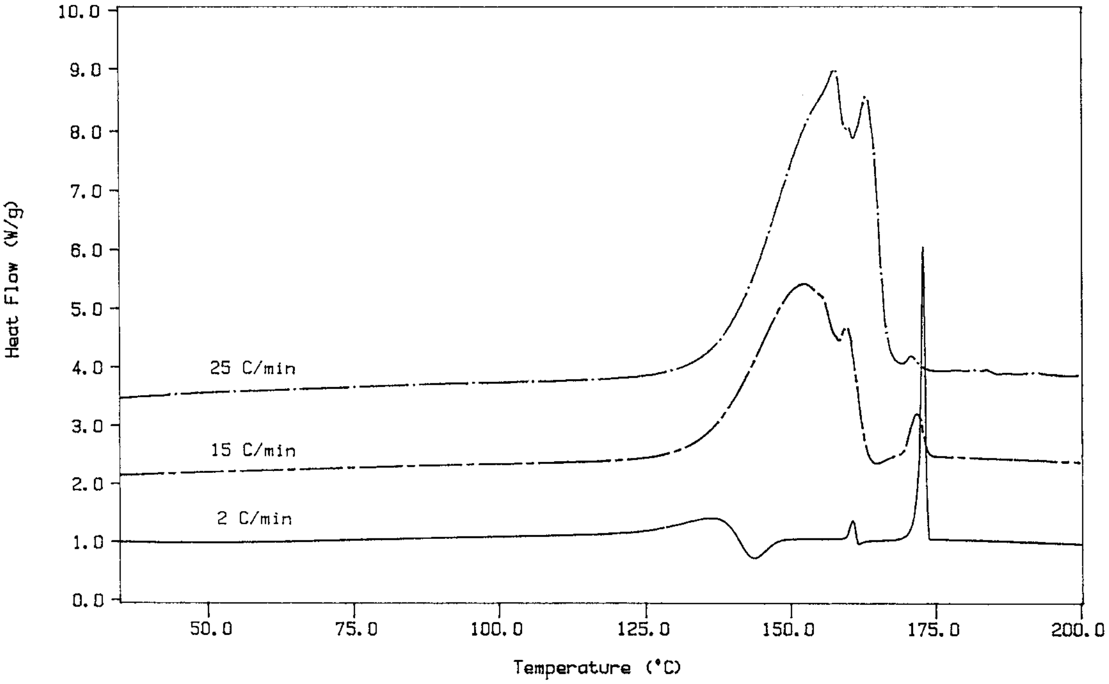

Fig. 3. The DSC curves for glucopyranosylmannitol-ethanol (2/1) measured with heating rates of 2, 15 and 25°C min^{-1}.

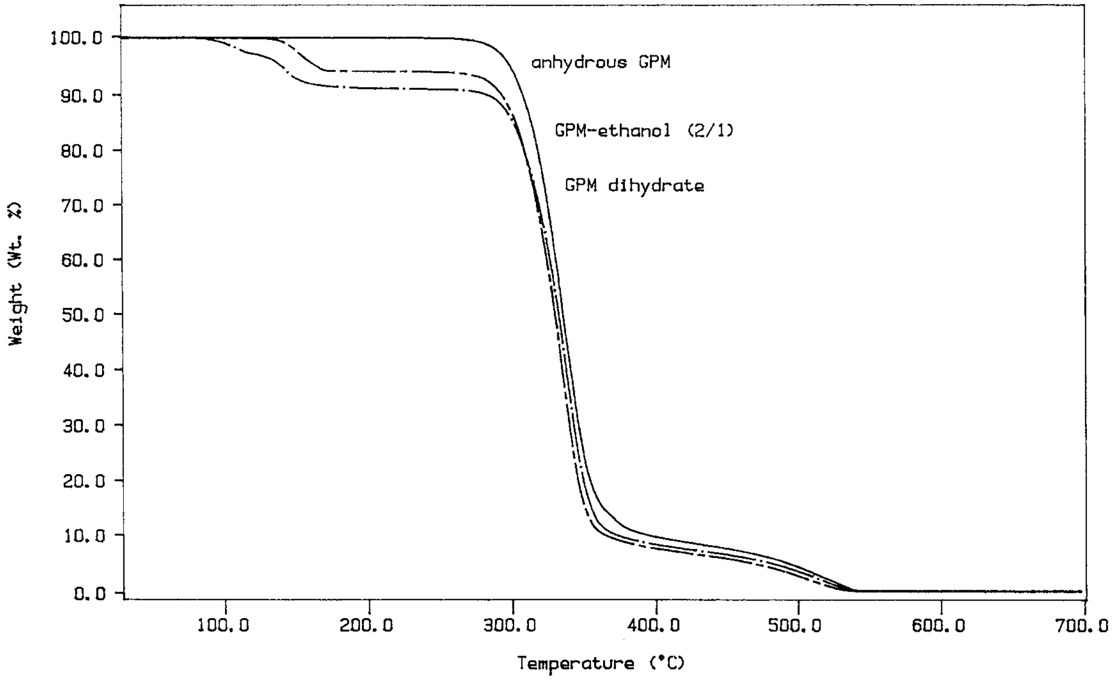

Fig. 4. The TG curves for anhydrous glucopyranosylmannitol, glucopyranosylmannitol dihydrate and glucopyranosylmannitol-ethanol (2/1) measured with heating rate of 10°C min^{-1}.

glucopyranosylmannitol dihydrate is noticed. The DSC curves for glucopyranosylmannitol dihydrate measured with heating rates of 2, 5 and 15°C min^{-1} are in shown in Fig. 2. The melting peak and onset values for glucopyranosylmannitol monohydrate are 132.8 (19)°C and 132.9 (13)°C, respectively. These values are not very reliable, because the shape of the melting peak in the DSC curve is not ideal. This is the reason, why the extrapolated onset value is higher than the peak value for glucopyranosylmannitol monohydrate. The standard deviations for these peak and onset values are 2.53 and 1.70, and the correlation coefficients are 0.8117 and 0.5184, respectively.

The behaviour of glucopyranosylmannitol-ethanol (2/1) is very similar to that of glucopyranosylmannitol dihydrate. With low heating rates, the first endotherm noticed in the DSC curve is the partial evaporation of ethanol, followed by an exotherm caused by the

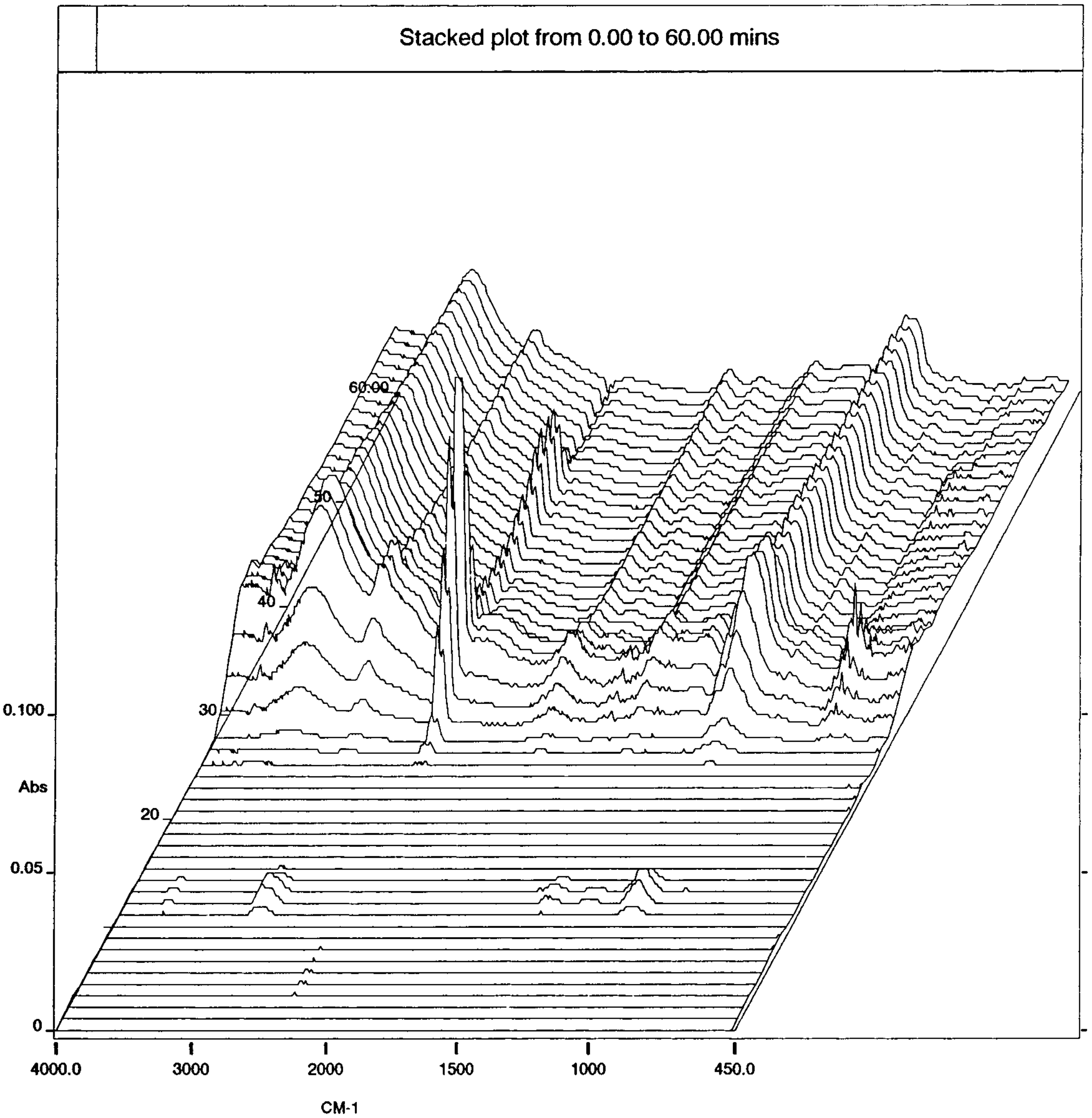

Fig. 5. The stacked plot of TG-FTIR measurement of glucopyranosylmannitol-ethanol (2/1).

recrystallization of anhydrous glucopyranosylmannitol. The second endotherm, thus, is caused by the melting of the glucopyranosylmannitol-ethanol (2/1) and the last endotherm is the melting peak of the anhydrous glucopyranosylmannitol formed during heating the sample. With higher heating rates, the melting endotherm of the anhydrous glucopyranosylmannitol is hardly noticed. The main peak in the DSC curves with high heating rates is the simultaneous evaporation of the ethanol molecule and the melting of glucopyranosylmannitol-ethanol (2/1). The DSC curves for glucopyranosylmannitol-ethanol (2/1) measured with heating rates of 2, 15 and 25°C min^{-1} are presented in Fig. 3.

3.2. TG-FTIR measurements

The TG curves measured with 10°C min^{-1} for anhydrous glucopyranosylmannitol, glucopyranosylmannitol dihydrate and glucopyranosylmannitol-ethanol (2/1) are in presented in Fig. 4. According to these measurements, glucopyranosylmannitol dihydrate loses its crystal water molecules easier than glucopyranosylmannitol-ethanol (2/1) loses its ethanol molecule. Glucopyranosylmannitol-ethanol (2/1) lost its ethanol molecule in the 110–190°C range (Δm_{meas}=6.0 wt%, Δm_{theor}=6.3 wt%) and glucopyranosylmannitol dihydrate lost its crystal water in the 60–210°C range (Δm_{meas}=9.3 wt%, $\Delta m_{\text{theor.}}$=9.5 wt%). The thermal decomposition of glucopyranosylmannitol dihydrate to anhydrous glucopyranosylmannitol takes place in two steps; the dihydrate loses its crystal water molecules one by one. With a heating rate of 0.5°C min^{-1}, this is clearly noticeable.

The volatile gases from the TG measurements were analyzed with FTIR. The removal of ethanol molecule from glucopyranosylmannitol-ethanol (2/1) can most

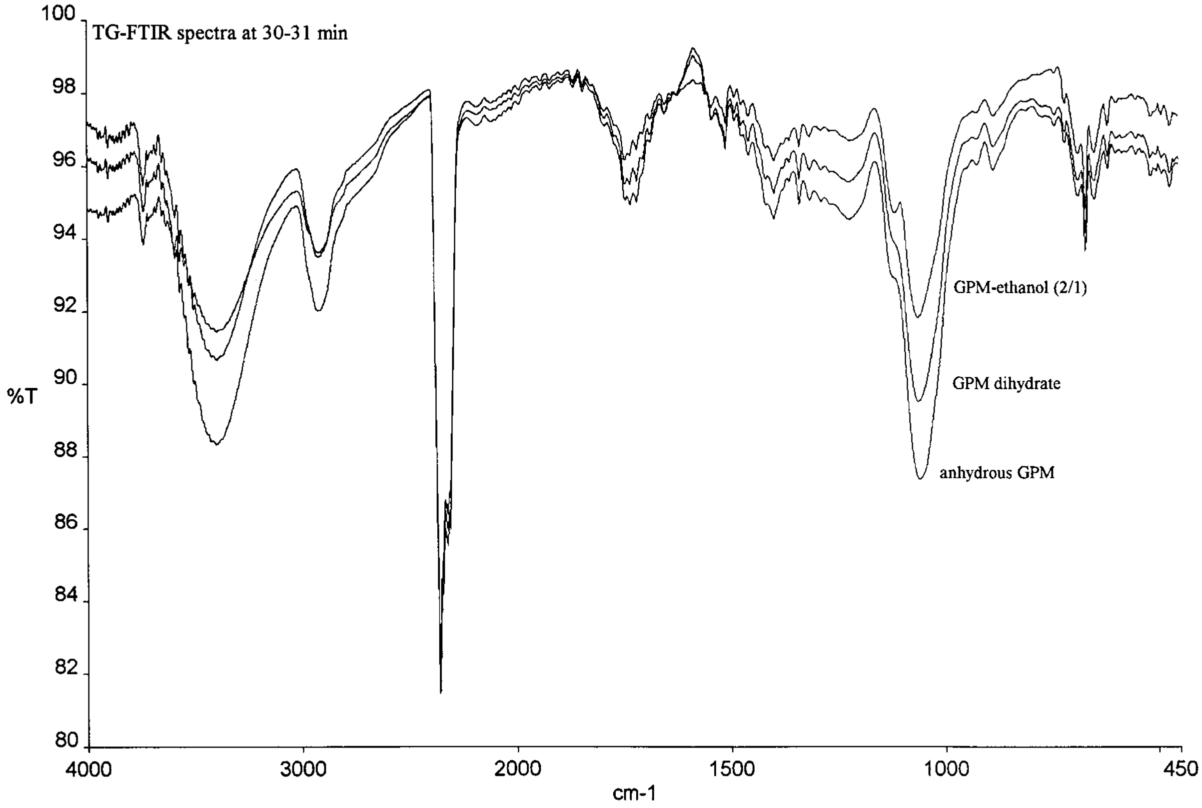

Fig. 6. The FTIR spectra of anhydrous glucopyranosylmannitol, glucopyranosylmannitol dihydrate and glucopyranosylmannitol-ethanol (2/1) at 30–31 min (330–340°C).

clearly be seen at 10–11 min (130–140°C) from the stacked plot of the TG-FTIR measurement in Fig. 5.

After the evaporation of ethanol molecule from glucopyranosylmannitol-ethanol (2/1) and the evaporation of crystal water molecules in glucopyranosylmannitol dihydrate the decomposition products for anhydrous glucopyranosylmannitol, glucopyranosylmannitol dihydrate and glucopyranosylmannitol-ethanol (2/1) are very similar, as can be noticed from the FTIR spectra at 30–31 min (330–340°C) in Fig. 6. The main decomposition products are carbon dioxide (noticed as sharp and intensive peak at 2360 cm^{-1} and a smaller peak at 671 cm^{-1}), water (noticed from several peaks in a region of 2000–1300 cm^{-1}) and some carbon compounds containing OH-groups (noticed from broad peak at 3396 cm^{-1} and at ca. 1061 cm^{-1}). These OH-groups are hydrogen bonded, while the peaks are very broad.

4. Discussion

The melting peak and onset values for anhydrous glucopyranosylmannitol can be determined most reliably with DSC by measuring at different heating rates and using linear regression to extrapolate the heating rate to isothermal situation. Glucopyranosylmannitol dihydrate and glucopyranosylmannitol-ethanol (2/1) obtain monotropic polymorphism and, thus, the results obtained for them are not so reliable because they decompose to other compounds during measurements. An intermediate compound, glucopyranosylmannitol monohydrate, is observed from the TG and DSC curves of glucopyranosylmannitol dihydrate.

The TG-FTIR measurements are of a great value in the identification of glucopyranosylmannitol-ethanol (2/1) as the loss of the ethanol molecule is clearly seen in the FTIR spectrum in the 130–140°C range.

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