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Determination of the degree of substitution of hydroxypropyl guar gum at C-6 by Pyrolysis-Gas Chromatography spectrometry

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ABSTRACT

Determination of the degree of substitution of hydroxypropyl guar gum is important as it provides information about the inhomogeneous substitution that may seriously affect the properties in various applications. In this study, the pyrolysis products of guar gum and hydroxypropyl guar gums were examined by gas chromatography and GC–MS spectrometry. Results showed that 1,2-propanediol was the product of hydroxypropyl at C-6 which splitted from the monosaccharide. Hydroxypropyl guar gums were analyzed to determine the degree of substitution at C-6, and the values were in good agreement with the values obtained by other methods. The present method is used to determine the degree of substitution at C-6 of hydroxyethyl guar gum. The present method is reliable, sensitive, and easy to operate, which provides a new way to characterize the degree of substitution at C-6 for hydroxypropyl and hydroxyethyl guar gum.

1. Introduction

Guar gum (GG) consisting of a 1,4-linked β-D-mannopyranose backbone with the branches of 1,6-linked β-D-galactopyranose and its derivatives with various functional groups hold important potential applications in numerous industries such as food, paints and pigments, oil field, mining, paper, water treatment, personal care, pharmaceutical and agriculture (McCleary, Clark, Dea, & David, 1985). Hydroxypropyl guar gum (HPG) is one of the most used derivatives. Compared with native guar gum, the HPG has better solubility and thermal stability in solution. HPG is prepared from the native guar gum via an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst (Lapasin, De Lorenzi, Pricl, & Torriano, 1995). The chemical and functional properties of HPG are mainly dependent on the pattern of substitution and the distribution of substituent (Floyd, Kohler, & Ward, 1972). The degree of molar substitution (MS) measures the number of moles of combined propylene oxide per monosaccharide unit. The MS of HPG can be determined by means of ^{1}H NMR or ^{13}C NMR, however, the NMR method cannot give any information on the degree of substitution of individual hydroxyls of the glucose units due to the low resolution and difficulties of NMR spectral resonances assignment. Several analytical methods have been developed over the years for the determination of the distribution of substituents of the hydroxypropyl group. Gas–liquid chromatography with mass spectrometry (GLC–MS) was also used to determine the substituent distribution in hydroxypropylated potato amylopectin starch (Richardson, Nilsson, Bergquist, Gorton, & Mischnick, 2000). This procedure was employed as the standard method of testing, however, it was troublesome and time-consuming.

In this study, the degree of substitution at C-6 was determined by Pyrolysis-Gas Chromatography–Mass Spectrometry. 1,2-Propanediol was the product of hydroxypropyl which substituted at C-6 from the monosaccharide. Hydroxypropyl guar gums with different molar substitution were analyzed to determine the degree of substitution at C-6, the values of the degree of substitution at C-6 were in good agreement with selective oxidation (Ye et al., 2009). This method is reliable, sensitive, quick, and easy to operate, which provides a new way to determine the degree of substitution at C-6 for hydroxyethyl and hydroxypropyl substituted polysaccharides.

2. Experimental

2.1. Materials

Guar gum (GG) and hydroxypropyl guar gums (HPGs) with different MS were kindly provided by the Jingkun Oilfield Chemistry Company, Jiangsu in China. The Mn value of guar gum was 2.5×10^6 g/mol. The average molecular weight of samples was determined by gel permeation chromatography (GPC) with a Shimadzu Instrument. The MS of HPGs were determined by ^{1}H NMR spectroscopy. All other reagents are all analytical grade.

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Table 1
Analytical result of the main pyrolytic liquid of guar gum, hydroxypropyl guar gum with low degree of substitution (HPG-1), hydroxypropyl guar gum with high degree of substitution (HPG-4).

Retention time (min)	Pyrolysis compounds	Similarity	Relative content (%)		
			Guar gum	HPG-1	HPG-4
1.928	Acetic acid	90	15.495	17.422	
2.350	1-Hydroxy-2-propanone	80	18.694	7.811	17.977
3.483	1,2-Propanediol	86		9.729	79.658
5.654	2-Furancarboxaldehyde	91	11.229	41.272	
6.366	2-Furanmethanol	90	6.855		
9.353	5-Methyl-2-furancarboxaldehyde	87	7.164	0.765	

2.2. Pretreatment of samples

Guar gum and hydroxypropyl guar gums were purified by dissolving in water and precipitated from solution with the addition of ethanol.

2.3. Pyrolysis of GG and HPG

The pyrolysis of the samples was performed in pipe furnace. Samples were heated from 20 °C to 320 °C, and then kept for 1 h. The temperature ramp was 10 °C/min controlled with Temperature Control Specialists (SKW-1000). The pyrolysis products were collected in an ice trap and analyzed by gas chromatography–mass spectrometry (Agilent 5973N GC/MS: column, HP-Innowax; inlet temp., 250 °C; detector temp., 250 °C; He flow, 40 mL/min; a split ratio, 50:1). Experimental parameters for GC/MS were identical and included the following: initial temperature, 40 °C; initial time, 2 min; program rate, 10 °C/min; final temperature, 180 °C; and then kept for 4 min; the solvent delay time, 2.2 min. The pyrolysis products was also analyzed by gas chromatography (GC4000: column, HP-FFAP; inlet temp., 250 °C; detector temp., 280 °C; N_2 flow, 40 mL/min). Experimental parameters for GC were identical and included the following: initial temperature, 70 °C; initial time, 7 min; program rate, 20 °C/min; final temperature, 210 °C; and then kept for 5 min; 2.0 g/L methanol aqueous solution was used as internal standard to determine the concentration of 1,2-propanediol. The pyrolysis of each sample was repeated 5 times, and the average value was used for final analysis.

3. Results and discussion

3.1. Qualitative analysis of pyrolytic liquid

The compositions of the main components of the pyrolytic liquid obtained from GG and HPG-1, HPG-2, HPG-3, HPG-4 determined by GC/MS are given in Table 1. The MS of HPG-1, HPG-2, HPG-3, HPG-4 were 0.14, 0.36, 0.51, 1.54 respectively (Table 1).

The pyrolysis products of these samples contains mainly 1,2-propanediol, 5-methyl-2-furancarboxaldehyde, 2-furancarboxaldehyde and 1-hydroxy-2-propanone. The concentration of 1,2-propanediol increases with MS of HPGs. 1,2-Propanediol cannot be detected in the pyrolytic liquid obtained from pure guar gum. The contain of 5-methyl-2-furancarboxaldehyde and 2-furancarboxaldehyde which are the main components of the pyrolytic liquid obtained from GG (Zhang et al., 2010) decrease with the increase of MS of HPGs, and which become undetectable in the pyrolytic liquid obtained from the HPG with high degree of substitution.

3.2. Analysis of the mechanism of the pyrolysis of GG and HPG

TGA and DTA curves of the original guar gum show the onset and endset temperatures are 230 °C and 310 °C respectively (Varmao, Kokane, Pathakb, & Pradhad, 1996), so the pyrolysis temperature was adjusted to 320 °C. The formation of anhydrosugars is the first step in the formation of volatile compounds from the pyrolysis of carbohydrate polymers (Piskorz, Radlein, & Scott, 1986). Because the bond length of C-6 to O is longer than C-2 to O and C-3 to O, levoglucosan (1,6-anhydro-β-D-glucopyranose) which is a significant intermediate product in the decomposition of guar gum is formed by dehydration. Levoglucosan is formed by stripping of 1,2-propanediol (Fig. 1).

The cleavage of the glucosidic linkages is followed by ring opening at the ring glucosidic linkage to form two-carbon and four-carbon fragments with the two-carbon moiety rearranging to glycolaldehyde. Other compounds were postulated to form from various rearrangements of the four-carbon fragments (Lipska & Wodley, 1969).

Furan compounds are generally formed from the dehydration of carbohydrates and are not very likely to involve recombinations of the sugar fragments. On this basis 2-furaldehyde could have been derived either from the first or the last five carbons of the anhydro sugar. Formation of 2-furaldehyde from C-1 to C-5 is consistent with the degradation pathway of carbohydrates involving the conversion of the enolic forms of intermediate 3-deoxyglycosuloses to

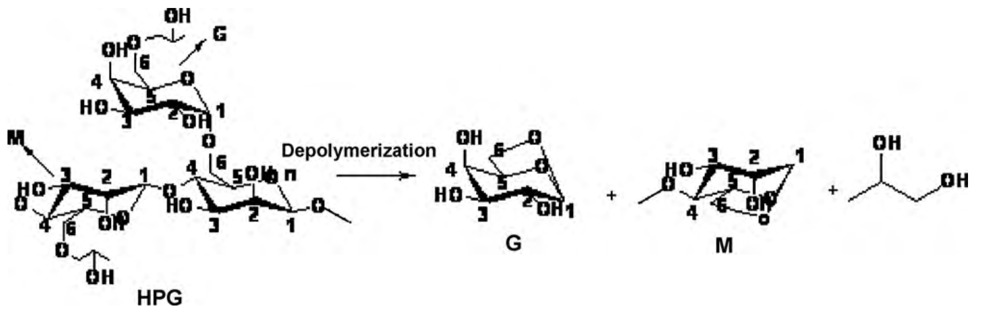

Fig. 1. Depolymerization mechanism of hydroxypropyl guar gum.

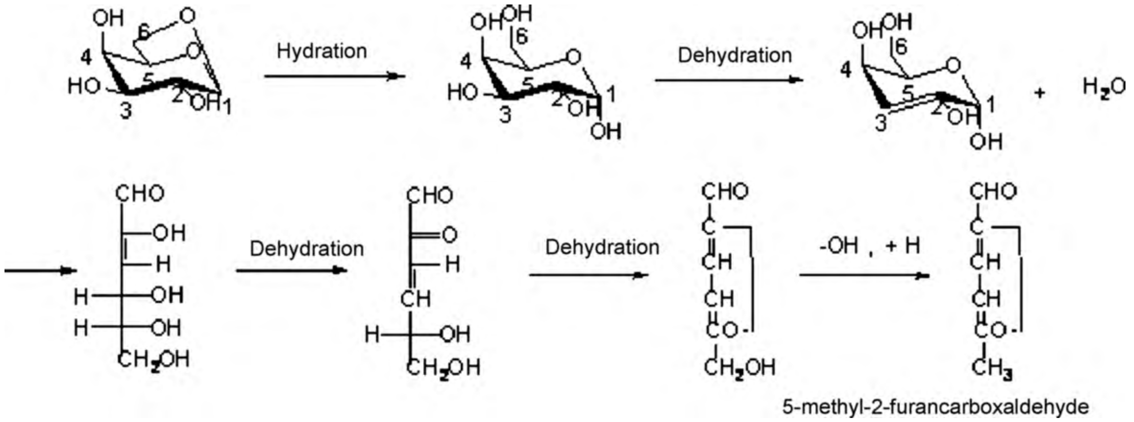

Fig. 2. Formation mechanism of 5-methyl-2-furancarboxaldehyde.

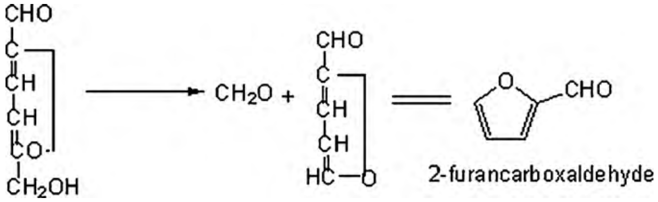

Fig. 3. Formation mechanism of 2-furancarboxaldehyde.

furan compounds (Shafizadeh & Lai, 1972) (Fig. 2). It is also consistent with the observations of Kato and Komorita (1968), who have identified 3-deoxyglycosuloses among the pyrolysis products of cellulose, D-glucose, D-fructose, and D-xylose and have shown that 5-(hydroxymethyl)-2-furaldehyde could form 2-furaldehyde (Fig. 3).

Bond lengths for the C-2 to C-3 bond and for the C-l to O-ring linkage are slightly greater than for other similar bonds, and the C–O bonds are thermally less stable than C–C bonds. These small differences lend support to the hypothesis that initial ring cleavage of the monosaccharide tends to occur most frequently at these two locations, yielding a two-carbon fragment and a four-carbon fragment, the two-carbon fragment rearranging to a relatively stable product, hydroxyacetaldehyde, while the four-carbon fragment can undergo a number of dehydration, rearrangement, decarbonylation reactions to yield 1-hydroxy-2-propanone (Fig. 4).

When the hydroxyl groups at C-2 or C-3 were substituted by hydroxypropyl, dehydration process cannot be followed as showed in Fig. 2, the content of 5-methyl-2-furancarboxaldehyde and 2-furancarboxaldehyde decrease with the increase of MS as showed in Table 1. 5-Methyl-2-furancarboxaldehyde and 2-furancarboxaldehyde are the main components of the pyrolytic liquid obtained from pure guar gum. Small amount of 5-methyl-2-furancarboxaldehyde and 2-furancarboxaldehyde can be detected in pyrolytic liquid obtained from hydroxypropyl guar gum with low degree of substitution, because most of the –OH groups in guar gum were not substituted by hydroxypropyl and the dehydration can be followed partially as showed in Fig. 2. 5-Methyl-2-furancarboxaldehyde and 2-furancarboxaldehyde cannot be detected in pyrolytic liquid obtained from hydroxypropyl guar gum with high degree of substitution ($MS > 1$), because the pattern of substitution is mono-substituted mainly and each monosaccharide unit is almost substituted, the dehydration cannot be followed as showed in Fig. 2. 1-Hydroxy-2-propanone is formed from the cleavage of C-1 to O and C-2 to C-3, then 1-hydroxy-2-propanone can be detected in all samples as showed in Table 1. Under the conditions guar gum degrades by eliminations of hydroxyl groups yielding substantial amounts of water and char. The hydroxypropyl substituted at C-2 or C-3 is remained in the form of char, because the production rate of char ($m_{\text{char}}/m_{\text{sample}}$) is proportional to ($1 - DS_6/MS$) approximatively, and the linear correlation coefficient is 0.92.

3.3. Calculation of degree of substitution at C-6

It is difficult to collect completely all the 1,2-propanediol produced during the experimental process, the recovery rate (χ) of 1,2-propanediol must be determined. The pyrolysis of the mixture of 0.15 g 1,2-propanediol and 1.86 g guar gum was performed in the same experimental condition, and the amount of 1,2-propanediol produced was determined. The recovery rate (χ) was determined with an average value of 86.6%. The concentration of 1,2-propanediol was determined by GC, and methanol aqueous solution was used as internal standard (Table 2).

$$DS_6 = \frac{n_P/\chi}{m_{HPG}/M_{HPG}}$$

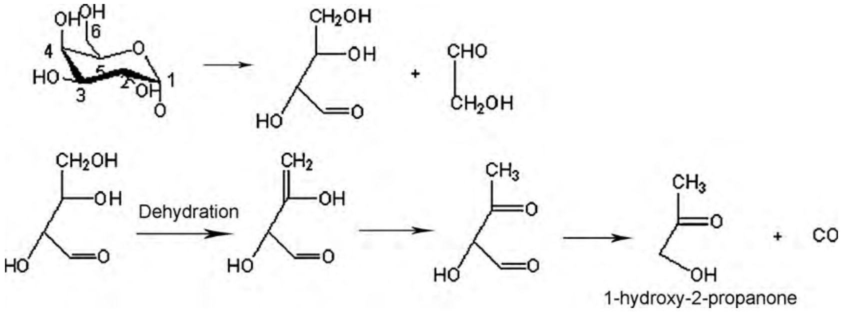

Fig. 4. Formation mechanism of 1-hydroxy-2-propanone.

Table 2
DS_6 of HPGs with different MS by two methods.

Sample	MS	M_S (g)	M_P (g)	n_P:n_{HPG}	DS_6^a	RSD (%) ($n = 5$)	DS_6^b
HPG-1	0.14	2.0783	0.0407	0.04	0.05	6.0	0.05
HPG-2	0.36	2.0226	0.1037	0.12	0.14	3.6	0.18
HPG-3	0.51	2.0542	0.1482	0.17	0.20	4.4	0.19
HPG-4	1.54	2.0215	0.2194	0.35	0.40	5.2	0.39

MS was determined by ^{1}H NMR, DS_6^a was determined by this method, DS_6^b was determined by periodate oxidation.

Table 3
DS_6 of HEGs with different MS by two methods.

Sample	MS	$n_{ethanediol}$:n_{HPG}	DS_6^a	RSD (%) ($n = 5$)	DS_6^b
HEG-1	0.39	0.20	0.23	2.8	0.23
HEG-2	0.47	0.27	0.32	1.7	0.28
HEG-3	1.08	0.45	0.53	3.1	0.53

MS was determined by cleavage of ether bonds of HEG (He, Jiang, & Wang, 2008), DS_6^a was determined by this method, DS_6^b was determined by TEMPO-mediated selective oxidation of HEG (Yin et al., 2008).

$M_{HPG} = 162 + 59 \times MS$; χ—the recovery rate (0.8658); n_P—the amount of substance of 1,2-propanediol; M_{HPG}—molecular weight of HPG unit; m_{HPG}—weight of HPG.

The values of the degree of substitution at C-6 were in good agreement with periodate oxidation, which shows the present method is reliable. The degree of substitution at C-6 of the hydrolyzed hydroxypropyl guar gum was also determined by this method, and the values were in good agreement with non-hydrolyzed hydroxypropyl guar gum. This indicated that molecular weight had no influence on the determination.

This method is extended to determine the degree of substitution at C-6 of hydroxyethyl guar gum. Because the NMR method cannot give any information on the degree of substitution of hydroxyethyl guar gum due to the low resolution and difficulties of NMR spectral resonances assignment. According to the mechanism of the pyrolysis of GG and HPG, ethanediol is the product of hydroxyethyl which substituted at C-6 from the monosaccharide (Table 3).

The values of the degree of substitution at C-6 were in good agreement with TEMPO-mediated selective oxidation of HEG, which shows the present method is reliable to determine the degree of substitution of hydroxyethyl at C-6.

4. Conclusion

In conclusion, the present technique using Pyrolysis-Gas Chromatography has proved to be a convenient and reliable chemical method to determine the degree of substitution at C-6 for hydroxyethyl and hydroxypropyl substituted polysaccharides. The results are in good agreement with the values found in the literature by other methods.

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