

## A simple non-aqueous method for carboxymethylation of galactomannans<sup>☆</sup>

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### Abstract

A simple non-aqueous method for the preparation of carboxymethyl (CM) derivatives of galactomannans and other biopolymers has been developed. Galactomannans such as guar, tara and locust bean gums were subjected to carboxymethylation using monochloroacetic acid under the catalytic influence of NaHCO<sub>3</sub> in dry state. The ratios of reagent and catalyst as well as the temperature and duration of the reaction were varied to prepare CM derivatives of different DS values ranging from 0.065 to 0.675. The progress of the reaction was followed by FT-IR and <sup>13</sup>C NMR spectral data. The reaction carried out in the presence of a small amount (<0.01%) of EtOH (just to surface wet the gum powder) gave CM derivatives having relatively a higher viscosity (3500 cps) than the unmodified gum. Being a mild alkali, removal of NaHCO<sub>3</sub> was easier, and the possibility of alkaline degradation caused by strong NaOH and also the effect of elevated temperature could be minimized. Overall the described method adds to the cost effectiveness as well as eco-friendly characteristic of the reaction.

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### 1. Introduction

Galactomannans, the polysaccharides found especially in the endosperm of several leguminous seeds, are composed of a mannan backbone linked together by β-(1→4) glycosidic linkages and having galactose side chain residues linked α-(1→6) (Dea and Morrison, 1975). Their solubility in water is mainly due to the presence of the latter. These semi rigid polymers with a persistent chain length in the range of 100 Å are found to be good thickening and stabilizing agents. Industrially viable and the most commonly used galactomannans are from guar (*Cyamopsis tetragonoloba*) (Davidson, 1980), tara (*Caesalpinia spinosa*) (Beak, 1977) and locust bean gum (*Ceratonia*

*siliqua*), which differ in the ratio of galactose to mannose, viz. 1:2, 1:3 and 1:4, respectively. Chemical modifications of polysaccharides by etherification, esterification, oxidation and hydroxypropylation (Sierakowaski, Milas, Desbrieres, & Rinacedo, 2000) are generally done for preparing custom-made derivatives having desirable functionality attributes. Carboxymethylation (CM) generally increases the hydrophilicity and solution clarity of the polysaccharide and makes it better soluble in aqueous systems. In a majority of the reported methods, carboxymethylation is done using strong NaOH and monochloroacetic acid (MCA) in aqueous medium at elevated temperature (Green, 1963; Moe, 1951; Yuch, 1972). Inadvertent molecular as well as reagent degradations induced by strong alkaline pH at elevated temperature cannot be underestimated under such conditions. No information is available on such reactions being carried out in absolutely dry, anhydrous conditions (without the addition of external water) at ambient or slightly elevated temperatures. The present study was carried out to fill in this gap.

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## 2. Experimental

### 2.1. Materials

Guar gum and tara gum were commercial food grade samples procured from Aqualon (Wilmington, DE, USA). Locust bean gum (food grade), cornstarch, monochloroacetic acid (MCA) and  $\text{NaHCO}_3$  were from Sigma Chemical Co., Mo, USA. The various other chemicals used were of analytical reagent quality. Total sugars were determined by phenol–sulphuric acid (Rao and Pattabhiraman, 1989) and reducing sugars by DNS method (Miller, 1959). The sugar composition was determined by acid depolymerization followed by alditol acetate derivatization and GLC (Soltzberg, 1970). A Shimadzu gas chromatograph equipped with FID and an OV-225 ss column (3% on Chromosorb W (100–120 mesh), 5 ft  $\times$  1/8") operated at 200 °C, with  $\text{N}_2$  as the carrier gas was used.

### 2.2. Carboxymethylation

In a typical reaction, to weighed samples (0.1–1 g) of galactomannan and finely powdered  $\text{NaHCO}_3$  (1–5 g) mixed well manually using a pestle and mortar, were added  $\sim$ 0.1–0.2 ml of ethanol (100% for surface wetting), and solid MCA (0.5–2 g). The reaction was carried out at ambient or elevated temperature (60, 80, 98 °C) for 2 h, with intermittent manual mixing with a glass rod, followed by the addition of dilute acetic acid to phenolphthalein end point. The salts (Green, 1963) formed were removed by repeated washings with 70% aqueous ethanol (3  $\times$  10 ml, kept for 15 min) followed by 100% ethanol and solvent exchange drying. The derivatized gums tested for  $\text{Na}^+$  using uranyl magnesium acetate (Vogel, 1989) spot test as well as AAS, were found to be completely free of  $\text{Na}^+$  ions, etc. by these washings. A number of CM derivatives of differing degree of substitution (DS) values were prepared by varying the ratio of catalyst and the reagent. In a similar way carboxymethylation was carried out without prior surface wetting with alcohol, and the derivatized dry products were recovered as mentioned above.

### 2.3. FT-IR spectroscopy

Both native and modified gum samples (5 mg) were blended with solid KBr, (100 mg, Sigma-Aldrich, USA) and about 40 mg of the blend was used to prepare a pellet (Delta press, Tetra Scientific, USA). The spectra were scanned from 4000 to 400  $\text{cm}^{-1}$  in a Perkin Elmer 2000 FT-IR spectrometer under dry air at room temperature.

### 2.4. DS by FT-IR spectroscopy

The degree of carboxymethylation was quantitatively determined by calculating the ratio between the intensity of hydrogen bonded –OH groups at about 3400  $\text{cm}^{-1}$  and the

intensity of carboxyl –C=O stretching of ether at 1740–1745  $\text{cm}^{-1}$ .  $\text{DS} = A_{1740-1745 \text{ cm}^{-1}}/A_{3400 \text{ cm}^{-1}}$  ( $A$  is intensity of absorption) was calculated after suitable baseline drawing for these absorbances (Nahalka, Nahalkova, Germeiner, & Blanarik, 1993)

### 2.5. CP MAS $^{13}\text{C}$ NMR spectroscopy

For solid state CP MAS  $^{13}\text{C}$  NMR, approximately 300 mg of samples were inserted into the ceramic rotor on a Bruker DSX 300 spectrometer. The spectrum, at 75.5 MHz was recorded using the cross polarization pulse sequence, spun at 7.5 kHz magic angle. A contact time of 1 ms and a pulse repetition time of 5 s were used with more than 2000 scans accumulated for each sample.

## 3. Results and discussion

Carboxymethylation (CM) is the most commonly used chemical derivatization method to transform water insoluble polymeric materials into a water-soluble form. The Williamson's etherification reaction carried out invariably in aqueous medium using strong NaOH and MCA at elevated temperature for different periods of time may lead to non-specific degradation by  $\beta$ -elimination and/or peeling reaction initiated at the reducing sugar unit due to high alkaline pH (Whistler and BeMiller, 1958), which in turn reduces the molecular weight of derivatized material. Reduction in solution viscosity, due to subtle disturbances in the water–macromolecule interaction is also reported for polysaccharides in the presence of high alkaline pH. Guar gum, even in oxygen-free alkaline solution is reported to generate saccharinic acids (Whistler and BeMiller, 1958).

CM reaction is highly dependent on several factors including the ratio of base catalyst, MCA, reaction medium, time and temperature. Hence, attempts were made to carryout the reaction (Fig. 1) in anhydrous conditions (without using external water) using solid  $\text{NaHCO}_3$ , a permitted food grade chemical, at both ambient as well as slightly elevated temperatures (Table 1). It was observed that as the concentration of base was increased beyond a ratio of 1.0, both solution viscosity as well as DS of the CM derivative were seriously affected, both showed a decreasing trend. Guar gum showed a relatively better DS, which increased slowly as the temperature was increased, but latter it decreased (Fig. 2). The reaction took place to some extent even at room temperature for extended period of time. The decrease in viscosity of CM guar was more as the temperature and catalyst concentration was increased.

In the case of tara gum a different trend in DS was noticed (Fig. 2), as the temperature was increased, the DS was increased, which then slightly decreased but later further increased. However, an increase in MCA concentration though did not change the DS that significantly, but gave products with considerable retention of viscosity.

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