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Short Communication

Macromolecular and functional properties of galactomannan from mesquite seed (*Prosopis glandulosa*)

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ABSTRACT

In this work, galactomannans from *Prosopis glandulosa* seeds were evaluated for their chemical composition and functional properties for potential industrial applications. In addition, those characteristics were compared with the commercial galactomannan guar gum. Mannose and galactose were the two most abundant carbohydrates present in *P. glandulosa* seeds, which represent 95.32% of total carbohydrates present in this material. Galactomannans from mesquite seed (GMS) yield was 16.53% and presented a M/G ratio of 2:1, which was higher than value observed for guar gum (1.6:1). The results obtained from functional properties showed that GMS has considerable potential to be considered as a food additive.

1. Introduction

The galactomannans are polysaccharides found as principal storage compounds in several endospermic seeds. They have a backbone chain of manose moieties linked by β-1,4 glycosidic linkages, which is substituted with single units of galactose linked α-1,6 to mannose backbone chain (Buckeridge, 2010). Some species of mesquite (*Prosopis* spp.) have been suggested as a source of galactomanan. The species receiving most attention have been *P. juliflora*, *P. chilensis*, *P. pallida* and *P. flexuosa* which are widely distributed through South America. *P. glandulosa* is another mesquite variety that grows naturally in Northern Mexico. It is resistant to arid conditions and has good nitrogen-fixing capacity (Chaires-Martínez, Salazar-Montoya, & Ramos-Ramírez, 2008). In a traditional way, mesquite pods were used as nutritional complement and for alcoholic and non-alcoholic beverage production due to their high sugar contents (Prokopiuk, Cruz, Grados, Garro, & Chiralt, 2000). In addition, seeds can be used as a galactomannan source for possible industry applications. Due to their structural features and non-toxicity, galactomannans have been used for different applications such as in low-fat cheese production (Hernández-Tinoco, Ramos-Ramírez, Falcony-Guajardo, & Salazar-Montoya, 2004), coatings and films formulation to extent the shelf-life of several tropical fruits (Cerqueira, Lima, Texeira, Moreira, & Vicente, 2009a). Usually, physicochemical and functional characteristics of galactomannans depend on mannose/galactose (M/G) ratio, which basically is determined by source and method employed for the extraction of this kind of polysaccharides (Cerqueira et al., 2009b). There are some commercial galactomannans such as guar gum (GG); locust bean gum (LBG), tara gum (TG) and fenugreek gum (FG) which are used in food and pharmaceutical industries. They have high water-binding capacity and generate viscous solutions acting as good emulsifying agents, effective thickeners and stabilizers (Wu, Cui, Eskin, & Goff, 2009).

This study had as objective to determine the chemical composition and functional properties of GMS and to compare those features with a commercial galactomannan. In addition, this study aims to promote the sustainable exploitation of mesquite for industrial applications.

2. Materials and methods

2.1. GMS extraction and purification

Mesquite seeds were obtained from Germoplasm Center in Saltillo, Coahuila, Mexico. The GMS extraction was carried

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out following the methodology previously reported by Sciarini, Maldonado, Ribotta, Pérez, and León (2009) with slight modifications. Briefly, an aqueous suspension of mesquite seeds (1:25 w/v ratio) was heated at 100 °C for 1 h. After cooling at room temperature, the suspension was centrifuged at 10, 000 rpm for 10 min. The supernatant was collected and the pellet was resuspended in boiling water. This process was repeated twice. The supernatants were precipitated with ethanol 96% (v/v) and pellet containing the polymer was lyophilized. GMS purification was carried out using the methodology previously reported by Chaires-Martínez et al. (2008).

2.2. Chemical analysis

Moisture, ash, lipid and protein contents were determined by following the official procedures of AOAC (1990). Glycosyl composition was determined using 500 mg of each galactomannan by combined gas chromatography/mass spectrometry (GC/MS) of the per-*O*-trimethylsilyl (TMS) derivatives of the monosaccharide methyl glycosides produced from the sample by acidic methanolysis according to the methodology previously described by Merkle and Poppe (1994). GC/MS analysis of the TMS methyl glycosides was performed on a 6890N GC interfaced to a 5975B MSD, using a Supelco EC-1 fused silica capillary column (30 m × 0.25 mm ID).

2.3. Functional properties

Water absorption capacity (WAC) of GMS and GG (form Sigma–Aldrich-*Cyamopsis tetragonoloba*) was evaluated according to the methodology previously reported by Sciarini et al. (2009). Briefly, 0.5 g of the sample was placed in a tube and 20 ml of distilled water were added. The suspension was left to rest until the polymer was completely wet. After that, the sample was centrifuged at 5000 rpm for 10 min the supernatant was decanted and the weight of the hydrated polymer was registered. WAC was calculated by weight difference. For emulsifying capacity (EC), 40 ml of solutions at different concentrations of each galactomannan (0.1, 0.25 and 0.5%) were mixed with 4 ml of corn oil (Maizola®) the mixture was homogenized in a homogenizer (WiseTis® HG-15D-USA) for 1 min and then, the sample was centrifuged at 2500 rpm for 10 min. The EC was calculated as:

$$\%EC = \frac{E_v}{t_{vs}} * 100 \quad (1)$$

where E_v is the emulsion volume and t_{vs} is the total volume of the solution. In addition, stability of the emulsion at high temperature was estimated. For such analysis, the emulsions were placed in a water bath at 80 °C for 20 min. Then, the samples were centrifuged at 2500 rpm for 10 min.

Finally, the emulsion stability (ES) was calculated as:

$$\%ES = \frac{\boldsymbol{f_{ev}}}{\boldsymbol{i_{ev}}} * 100 \quad (2)$$

where f_{ev} is the final emulsion volume and i_{es} is the initial emulsion volume.

2.4. Molecular characterization

The determination of viscosity parameters was carried out with an Ostwald-Fensk capillary viscometer (series 200) at 26 ± 0.1 °C, using exactly 10 ml of solution. Solutions of GMS at 0.5% (w/w) were employed and a range of dilutions was made to get relative viscosity values $1.2 < \eta_r < 2.0$ which were considered to maintain those solutions into good linearity of extrapolation to zero concentration.

Table 1
Chemical composition of galactomannans from mesquite seed (GMS) and guar gum.

	GMS	guar gum
Moisture (%)	10 ± 0.0b	12 ± 0.0a
Ashes (%)	1.8 ± 0.2a	1.2 ± 0.2b
Lipid (%)	0.45 ± 0.051b	1.47 ± 0.33a
Protein (%)	0.55 ± 0.06b	0.64 ± 0.53a
WAC ($g\,g^{-1}$)	3.93 ± 0.41b	5.86 ± 0.81a

Different letters denote significant differences ($p < 0.05$).

Huggins–Kraemer plots of η_{sp}/C and ln η_r/C versus C were used to estimate intrinsic viscosity $[\eta]$, according to the equations below:

$$\eta_{sp} = [\eta] + \kappa_H[\eta]^2 C \quad (3)$$

$$ln\frac{(\eta_r)}{C} = [\eta] + \kappa_K[\eta]^2 C \quad (4)$$

were = η_{sp} = specific viscosity, η_r = relative viscosity; $[\eta]$ = intrinsic viscosity; C = polymer concentration; k_H = Huggins's constant and k_K = Kraemer's constant.

2.4.1. Viscosity average molecular mass (Mv)

Mv was obtained from the intrinsic viscosity using the Mark–Houwink equation given by Doublier and Launay (1981) for GG and modified by Gaisford, Harding, Mitchell, & Bradley (1986) taking into account the different values of M/G of the galactomannans studied.

$$[\eta] = 11.55x10^{-6}[(1-r)Mv]^{0.98} \quad (5)$$

where r represents galactose/(mannose + galactose) ratio and $[\eta]$ is expressed in dL g^{-1}.

2.5. Statistical analysis:

Data analysis was carried out using SAS® 9.0. Mean comparison of treatments was made with a Tukey multiple range test ($p < 0.05$).

3. Results and discussion

Galactomannans extraction yield from *P. glandulosa* seeds was 16.53%. Ibañez and Ferrero (2003), and Chaires-Martínez et al. (2008) reported an extraction yield of 13% of galactomannans from *P. flexuosa* and *P. pallida* seeds, using NaOH as extractor agent. Strong acid and alkali solutions can affect the polymerization degree of polysaccharides; in this sense, the differences in yields can be attributed to use of NaOH which could affect the galactomannan yield extraction. In other study, Sciarini et al. (2009) recovered 11.9% of galactomanans form *Gleditsia triacanthos* using a similar method to the one used in this study. Our results indicate that the extraction and purification processes used in this work were more efficient to obtain galactomannans than those reported previously (Chaires-Martínez et al., 2008; Dakia, Bleckerb, Roberta, Watheleta, & Paquota, 2008; Figueiró, Góes, Moreira, & Sombra, 2004; Ibañez and Ferrero, 2003)

Table 1 shows the results obtained for proximal chemical analysis of GMS and GG. It can be observed that GMS had less content of protein and lipids than GG. Absence or low contents of lipids and proteins are desirable for polysaccharides such as galactomannans, since it is related with the purity of the sample.

Sugar composition analysis is shown in Table 2. The major amount of sugar present in the samples corresponds to galactose and mannose, which represent 95.32 and 93.94% of the total carbohydrates present in GMS and GG respectively. Smaller quantities of other sugars such as glucose, arabinose, rhamnnose, xylose and

Table 2
Monosaccharide compositions of galactomannans from mesquite seed (GMS) and guar gum.

Sugar	GMS (g/100 g)	Guar gum (g/100 g)
Arabinose	0.40	1.58
Rhamnose	ND	0.19
Xylose	0.16	0.28
Galacturonic acid	0.36	ND
Mannose	63.08	58.06
Galactose	31.64	35.88
Glucose	0.62	0.86

Glycosyl composition was determined using 500 mg of each galactomannan.
ND = not detected.

galacturonic acid were observed in the analyzed samples. According to this analysis, 2:1 was the M/G ratio for GMS and 1.6:1 for GG. Smaller values of M/G ratio were reported for *P. pallida* (Chaires-Martínez et al., 2008) and similar for *P. flexuosa* (Ibañez and Ferrero, 2003).

WAC values are shown in Table 1. The highest values of WAC were observed for GMS. It has been reported that water-galactomannans interaction could be easier due to decreasing chain-to-chain interaction degree of the polysaccharide, when drastic conditions were used in the procedures to extract these hydrocolloids, which could cause the structural unfolding and the increasing of the branched proportion of the biopolymer (Sciarini et al., 2009).

Emulsifying capacity has been associated at high surface active polymers. However, it has been reported that surface activity is not the only factor determining the emulsion properties. Interfacial activities, molecular weight and interaction with small amounts of protein must also be considered (Wu et al., 2009; Dickinson, 2009). Fig. 1 shows the emulsifying capacity observed for GMS and GG. It can be observed that emulsifying capacity was dependent of galactomannan concentration. The highest emulsifying capacity was recorded at 0.5% for both GMS and GG. Nonetheless, significant differences ($p < 0.5$) were observed between samples of galactomannans. GMS presented higher emulsifying capacity (92 ± 1.64, 94 ± 0.72 and 100%) than GG at all tested concentration. Our findings are consistent with those reported by Sciarini et al. (2009) for galactomannans extracted from *G. triacanthos* seeds. They observed 100% of emulsifying capacity for samples extracted with hot water. On the other hand, in a relevant study of four commercial galactomannans, Wu et al. (2009) reported values of emulsifying capacity that ranged from 40 to 70%, which are lower than those reported in this study. This gives a perspective for further possible uses of the GMS in food formulation as an emulsifying agent.

Usually, emulsions are thermodynamically unstable at high temperatures. In this study the stability of the emulsions at 80 °C was evaluated and is shown in Fig. 2. Both GMS and GG had a good capacity for keeping the emulsions stable. The stability of the emulsions ranged from 95 ± 0.63 to 97.4 ± 0.74 and 94.2 ± 1.47 to 100 ± 0.77 for GMS and GG, respectively. However, no significant differences were observed across these ranges (Fig. 2), which suggest that emulsion stability is independent of polymer concentration for the concentration reported in this work. Similar behavior was reported for galactomannans extracted from *G. triacanthos* seeds (Sciarini et al., 2009). According to Dickinson (2009), in some

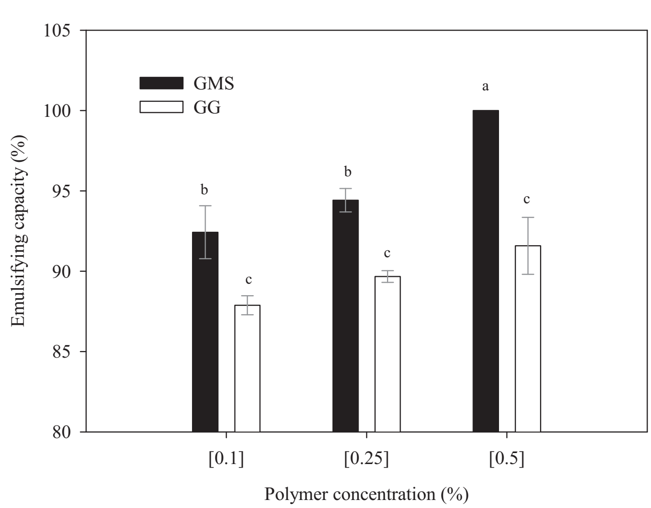

Fig. 1. Emulsifying capacity of galactomannans from mesquite seed (GMS) and guar gum (GG) as a function of polymer concentration.

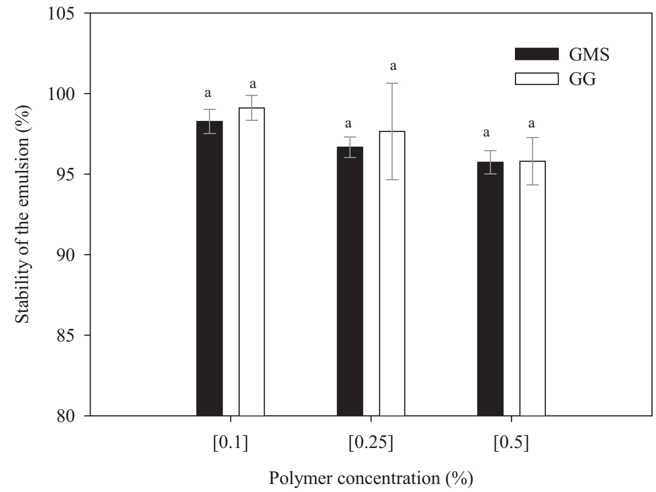

Fig. 2. Stability of the emulsion at 80 °C as a function of polymer concentration.

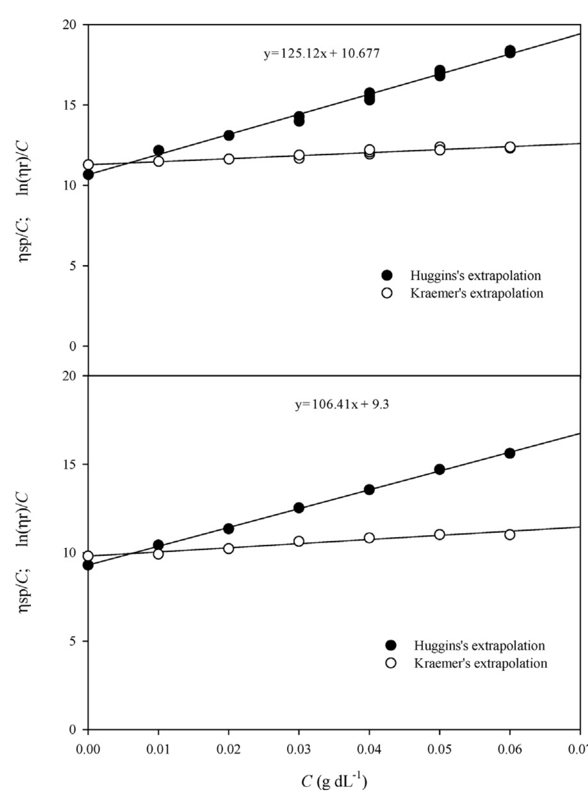

Fig. 3. The Mark–Houwink plot of the measured intrinsic viscosity data using Huggins and Kraemer's extrapolations, (a) GMS and (b) guar gum.

cases emulsifying stability does not depend of the emulsifier concentration, but hydrodynamic processes of droplet disruption have also influence on such property. That is, emulsion stability also depends on equipment and conditions employed for emulsion formation.

The values of intrinsic viscosity derived from relative viscosities of solutions with concentrations ranging from 0.01 to 0.07 g/dL by combined Huggins and Kramer extrapolation (Eqs. (3) and (4)) to infinite dilution ($C = 0$) were $[\langle \mathrm{eta} \rangle] = 11.0$ dL/g for GMS and $[\langle \mathrm{eta} \rangle] = 9.6$ dL/g for GG, giving viscosity-average molecular weights (Eq. (5)) of ~1.5 and ~1.4×10^6 Da, respectively (Fig. 3). Thus the extract from *P. glandulosa* has slightly higher solution viscosity and molecular weight than a typical sample of guar gum, which is used extensively as a commercial thickener.

4. Conclusions

The results obtained in chemical and functional properties and the macromolecular characterization of the hydrocolloid extracted from *P. glandulosa*, suggest that this polymer has great potential as a food additive especially as an emulsifier agent. However, further studies are required in order to understand the interactions between GMS and more complex systems.

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References

AOAC. (1990). *Official Methods for Analysis of the Association of Official Analytical Chemist* (15th ed., pp. 70). Arlington, VA: AOAC., 1011.

Buckeridge, M. S. (2010). Seed cell wall storage polysaccharides: Models to understand cell wall biosynthesis and degradation. *Plant Physiology*, *154*, 1017–1023.

Cerqueira, M. A., Lima, A. M., Texeira, J. A., Moreira, R. A., & Vicente, A. A. (2009). Suitability of novel galactomannans as edible coatings for tropical fruits. *Journal of Food Engineering*, *94*, 372–378.

Cerqueira, M. A., Pinheiro, A. C., Souza, B. W. S., Lima, A. M. P., Teixeira, J. A., Moreira, R. A., et al. (2009). Extraction, purification and characterization of galactomannans from non-traditional sources. *Carbohydrate Polymers*, *75*, 408–414.

Chaires-Martínez, L., Salazar-Montoya, J. A., & Ramos-Ramírez, E. G. (2008). Physico-chemical and functional characterization of the galactomannan obtained from mesquite seeds (*Prosopis pallida*). *European Food Research and Technology*, *227*, 1669–1676.

Dakia, P. A., Bleckerb, C., Roberta, C., Watheleta, B., & Paquota, M. (2008). Composition and physicochemical properties of locust bean gum extracted from whole seeds by acid or water dehulling pre-treatment. *Food Hydrocolloids*, *22*, 807–818.

Dickinson, E. (2009). Hydrocolloids as emulsifiers and emulsion stabilizers. *Food Hydrocolloids*, *23*, 1473–1482.

Doublier, J. D., & Launay, B. (1981). Rheology of galactomannan solutions: Comparative study of guar gum and locust bean gum. *Journal Texture Studies*, *12*, 151–172.

Figueiró, S. D., Góes, J. C., Moreira, R. A., & Sombra, A. S. B. (2004). On the physico-chemical and dielectric properties of glutaraldehyde crosslinked galactomannan–collagen films. *Carbohydrate Polymers*, *56*, 313–320.

Gaisford, S. E., Harding, S. E., Mitchell, J. R., & Bradley, T. D. (1986). A comparison between the hot and cold water soluble fraction of two locust bean gum samples. *Carbohydrate Polymers*, *6*, 423–442.

Hernández-Tinoco, A., Ramos-Ramírez, E. G., Falcony-Guajardo, C., & Salazar-Montoya, J. A. (2004). Rheometry and scanning electron microscopy study of casein curds added with mesquite seed gum and soy proteins. *Latin American Applied Research*, *34*, 195–202.

Ibañez, M. C., & Ferrero, C. (2003). Extraction and characterization of the hydrocolloid from *Prosopis flexuosa* DC seeds. *Food Research International*, *36*, 455–460.

Merkle, R. K., & Poppe, I. (1994). Carbohydrate composition analysis of glycoconjugates by gas–liquid chromatography/mass spectrometry. *Methods in Enzymology*, *230*, 1–15.

Prokopiuk, D., Cruz, G., Grados, N., Garro, O., & Chiralt, A. (2000). Estudio comparativo entre frutos de *Prosopis alba y Prosopis pallida*. *Multequina Latin American Journal of Natural Resources*, *9*, 35–45.

Sciarini, L. S., Maldonado, F., Ribotta, P. D., Pérez, G. T., & León, A. E. (2009). Chemical composition and functional properties of *Gleditsia triacanthos* gum. *Food Hydrocolloids*, *23*, 306–313.

Wu, Y., Cui, W., Eskin, N. A. M., & Goff, H. D. (2009). An investigation of four commercial galactomannans on their emulsion and rheological properties. *Food Research International*, *42*, 1141–1146.