Heliyon 10 (2024) e31421

Contents lists available at ScienceDirect

Heliyon

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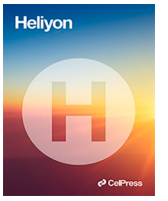

Research article

Enzyme-catalyzed transesterification of galactomannan extracted from mesquite seed (*Prosopis velutina*) with vinyl carboxylate esters

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ARTICLE INFO

Keywords:
Galactomannan ester
Enzymatic catalysis
Amphiphilic polysaccharides
Transesterification

ABSTRACT

Galactomannans (GM) are hemicellulosic polysaccharides composed of D-mannopyranose chains linked by β (1 → 4) glycosidic linkages with branches of D-galactopyranose linked by α (1 → 6) linkages. This polysaccharide is recognized for its hydrophilic character, as it is rich in hydroxyl groups (-OH). This chemical characteristic, combined with the absence of ionic charges, enables structural modifications such as transesterification of the fatty acid chains (FA), which provides a strategy for obtaining amphiphilic structures. The enzyme-catalyzed syntheses were carried out in DMSO with GM decanoate (GMD) and GM palmitate (GMP) at different molar ratios (0.5 and 1.0) and the resulting structures were evaluated with infrared spectroscopy (FTIR), solid-state nuclear magnetic resonance (CP/MAS ^{13}C NMR) and differential scanning calorimetry (DSC). The FTIR spectrum confirmed the transesterification of GM with the appearance of a C═O band (1730-1750 cm^{-1}). These results were confirmed by the signals observed at 177 and 30 ppm in the CP/MAS ^{13}C NMR spectrum, which corresponded to the C═O groups of the esters and the terminal –CH_3 groups of the FA chains, respectively. Finally, DSC showed glass transition temperatures (Tg) in the range 43–51 °C, while the melting temperatures (Tm) of the GM esters (59 °C) were not affected by different degrees of esterification (DE) for GMD (0.37 and 0.71) and GMP (0.47 and 0.57).

1. Introduction

Galactomannan (GM) is a multifunctional polysaccharide containing a D-mannopyranose main chain linked by β (1 → 4) glycosidic bonds and D-galactopyranose branches linked to the mannan main chain by α (1 → 6) bonds. Its composition and characteristics vary according to the source and the extraction procedures used [1]. GM can be distinguished from each other by the mannose/galactose ratio (M/G), which varies between approximately 1.2 and 3.5. Carob gum has an M/G ratio of 3.5 [2], the tara gum ratio is 3.0 [3],

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https://doi.org/10.1016/j.heliyon.2024.e31421
Received 18 December 2023; Received in revised form 14 May 2024; Accepted 15 May 2024
Available online 16 May 2024

those of guar and mesquite seed gums are 1.5 [4,5], and the fenugreek gum ratio is 1.2 [6]. The structural characteristics of these polysaccharides make them chemically and biochemically reactive and soluble in water over a wide temperature range.

Due to the large numbers of hydroxyl (-OH) groups and the absence of ionic charges in the structures, GM are susceptible to molecular changes [7]. Chemical modification has traditionally been used to change the hydrophilicity of a GM by forming esters to obtain amphiphilic structures. This structural change reduces hydrogen bonding between the polysaccharide chains and modifies the solubility and swelling properties [8]. Transesterification involves a reaction of a saccharide alcohol with an acylating agent, such as a vinyl carboxylate, acyl chloride, acid anhydride, and the carboxylic acid itself. Here, esters were obtained conventionally via strong acid catalysis (concentrated H_2SO_4) or by *in situ* activation of the carboxylic group under mild conditions for acylation of the polysaccharide. However, this process, apart from being unspecific, is also a huge generator of environmentally polluting waste [9].

In an alternative to this process, biocatalysis with enzymes has been used to modify GM structures, and this reaction shows regioselectivity for galactose *O*-6, which allows the syntheses of products with well-defined or stereospecific structures [10,11]. Some enzymes have broad substrate tolerances and catalyze the reactions of generic structures; hence, esterases, proteases, and lipases have been used to catalyze the formation of esters in polysaccharides, even though it is an unnatural function of the enzyme [12]. Therefore, the enzyme tends to react with –OH groups (esterification) or esters (hydrolysis) that are sterically accessible, i.e., those in primary positions [13].

Enzymes require at least a certain amount of water to carry out their functions correctly; however, water is not a good medium for transesterification because it is reversible under these conditions. When excess water is present, the reaction tends to favor hydrolysis, so the extent of substitution in the product is very low [14]. In contrast, polar aprotic solvents such as dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) remove the water from the enzyme surface, inactivating it and, therefore, lowering the hydrogen bonding capacity, leading to increased enzyme activity [11,15–17]. However, the protocols used to carry out transesterifications of galactomannans are not fully established. Therefore, in this work we report the synthesis of GM esters (decanoate and palmitate) catalyzed by Lipase B from *Candida antarctica* in an aprotic polar solvent and its chemical and physical characterization. This methodology represents an alternative with less environmental impact in its process and greater control in the efficiency of the esterification process.

2. Materials and methods

2.1. Materials

2.1.1. Obtaining galactomannan

Mature pods of *Prosopis velutina* were collected in June of 2021 in Baviacora, Sonora, Mexico, which is located between the geographic coordinates 29° 42′ 37˝north latitude and 110° 09′ 37˝west longitudes, at an average altitude of 553 m above sea level. The plant was identified by PhD A. Castro at Centro Interdisciplinario de Investigación para el Desarrollo Integral Regional, Unidad Durango, Mexico, Herbarium. The pods were dried in an oven at 60 °C for 24 h and manually selected, and those damaged by insects were discarded. The selected pods were mechanically broken with a hand mill, and the seeds were manually separated and used for GM extraction.

2.1.2. Reagents

Vinyl decanoate, dimethyl-sulfoxide (DMSO) and Lipase B from *Candida antarctica* were purchased from Sigma-Aldrich (St. Louis, MO, USA); vinyl palmitate stabilized with MEHQ was purchased from TCI America (Portland, OR, USA).

2.2. Methods

2.2.1. Extraction and characterization of galactomannans from Prosopis velutina

2.2.1.1. Galactomannan extraction and purification. For the GM extraction, the mesquite seeds were broken with a household coffee mill; thereafter, the endosperm was manually separated from the germ and the hull, and finally, the endosperm was suspended in double-distilled water at a proportion of 1:20 (w/v, endosperm:water) at 25 °C for 24 h. The sample suspended in water was filtered through gauze, and the solid residue was resuspended in distilled water and filtered again. The two filtrates were combined, and the hydrocolloids were recovered by precipitation with a liquid-absolute ethanol ratio of 1:1 (v/v). The precipitate was freeze-dried, ground, and weighed. This product was suspended in distilled water at 2.5 g/L with constant stirring at room temperature and then centrifuged at 3800 g (HERMLE Labortechnik, Model Z 300, Wehingen, Germany) for 20 min. The supernatant containing the GM was freeze-dried and stored in a dry place until further use.

2.2.1.2. Compositional analysis of the GM. The moisture content of the GM was determined gravimetrically by drying samples in a vacuum oven (VWR Scientific Inc., Model 1430, Logan Township, NJ, USA) at 80 °C for 4 h. The protein content was determined by the Bradford method. The total inorganic content was measured by incineration at 550 °C in a furnace oven for 8 h. The fat content was determined by time-domain nuclear magnetic resonance (TD-NMR) with a spin–echo pulse sequence with a duration of 3.5 msec between 100 90° and 180° pulses in a Bruker minispec mq20 analyzer at 20 MHz. The total carbohydrate content was calculated with the phenol–sulfuric DuBois method.

2.2.1.3. Nuclear magnetic resonance spectroscopy (^{1}H NMR). To determine the M/G ratio of the GM, high-resolution ^{1}H NMR spectroscopy of samples dissolved at 20 mg/mL in D_2O were obtained with a Bruker Avance 400 spectrometer (Billerica, MA, USA) operating at 400 MHz with a 90° pulse of 14.0 ms. The spectra were obtained at 70 °C [18].

2.2.1.4. Size exclusion chromatography - multi-angle laser light scattering (SEC-MALLS). The weight-average molar mass (Mw), number-average molar mass (Mn), polydispersity index (PDI) and intrinsic viscosity [ɳ] of the GM were determined. A size-exclusion chromatography (SEC) system and a DAWN HELOS-II 8 multiangle laser-light scattering (MALLS) detector coupled with a ViscoStar-II viscometer and a refractive index (RI) Optilab T-rex detector (Wyatt Technology Corp., Santa Barbara, CA, USA) were used. Briefly, a 5 mg sample of GM was dispersed in 1 mL of the mobile phase, stirred in a vortex for 10 s and then fixed at 80 °C for 1 h. Subsequently, the sample was cooled to room temperature and centrifuged at 15,000 rpm for 10 min. Finally, the sample was filtered through a 0.45 μm membrane before injection. An Agilent HPLC System (Agilent Technologies, Inc., Santa Clara, CA, USA) and Shodex OH-pak SBH-Q-804 and 805 columns (Shodex Showa Denco K·K., Tokyo, Japan) were used with flow rates of 0.5 mL/min (50 mM $NaNO_3$ solution containing 0.02 % NaN_3). The chromatograms were analyzed with Astra 6 software with a dn/dc value of 0.140 [19].

2.2.1.5. Solubility. Suspensions (20 mL) of GM (0.5 and 1 %, w/w) in water and DMSO were placed in water baths at 25° and 40 °C for 30 min with continuous stirring. The suspensions were then centrifuged at 800×*g* for 15 min. Ten mL aliquots of the supernatants were dried in a convection oven (Lindberg Blue M, Model MO1490A-1, Asheville NC, USA) at 100 °C for 12 h. The solubility was calculated as follows:

$$\%\ \text{Solubility} = \text{Wf} \times 20\ \text{Wi} \times 10 \times 100 \quad (1)$$

where Wi is the weight of GM used to prepare the suspensions, and Wf is the weight of the GM recovered from the solution [5].

2.2.2. Transesterification and characterization of the galactomannan esters

2.2.2.1. Galactomannan ester syntheses. The transesterification (Fig. 1) was carried out with 0.5 % solutions of GM in DMSO at 50 °C. Vinyl decanoate or vinyl palmitate were used as acyl donors and added in different molar proportions (0.5:1 and 1:1 FA:Gal) and then stirred for 2 h. Afterward, 20 U/mL of enzyme lipase B from *Candida antarctica* was added and reacted for 48 h at 250 rpm. The reaction was stopped by raising the temperature to 70 °C for 15 min for inactivation of the enzyme and evaporation of the byproducts of the reaction (acetaldehyde), and the system was immediately cooled in an ice bath. The GM ester was precipitated with 96 % ethanol at 4 °C and centrifuged at 10,000×*g* for 15 min at 4 °C. The supernatant was decanted, and two more washes were carried out with 96 % ethanol in the same way. Finally, these were dried in a vacuum oven at 60 °C.

2.2.2.2. Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR). The absorption spectra of GM, GMD, and GMP were obtained with a Nicolet iS50 infrared spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). The spectra were recorded in transmission mode from 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1}.

2.2.2.3. ^{13}C-CP/MAS NMR. The esterification degrees (DE) of GM were assessed with solid-state CP/MAS ^{13}C NMR spectra recorded on a Bruker Ascend 400 MHz NMR spectrometer (Karlsruhe, Germany). The chemical shifts (ppm) were referenced externally to the glycine signal at 176.5 ppm. Approximately 100 mg of the dry sample (GM, GMD, or GMP) was inserted into a ZrO_2 ceramic rotor. The cross-polarization sequence was utilized for all samples, which were spun at the magic angle at 10 kHz with a contact time of 1 ms and a pulse (repetition) time of 5 s, and more than 1000 scans were accumulated for each spectrum [20]. The DE of GMD and GMP realized with different molar ratios were determined from the CP/MAS NMR spectra. Taking into consideration the average of the sum of the relative areas (r) for the GM (C1–C5) and the average of the sum of those for the FA (C═O and –CH_3) from the following equation:

$$\text{DE} = \text{r FA/r GM}\ (0.45) \quad (2)$$

where 0.45 is the percentage of galactose contained in the GM [21].

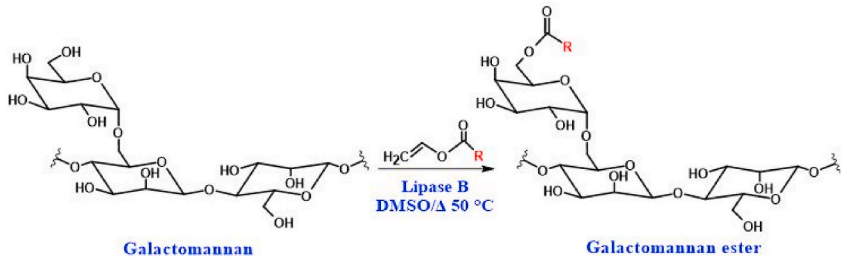

Fig. 1. Mechanism of GM transesterification catalyzed by *C. antarctica* lipase B in aprotic polar solvent (R: fatty acid chain).

2.2.2.4. Differential scanning calorimetry (DSC). A PerkinElmer (Diamond DSC7) calorimeter was used to determine the fusion temperatures (Tm) and vitreous temperatures (Tg) [5] of the GM, GMD and GMP. The polysaccharide samples (8–10 mg) were weighed into stainless steel pans, hermetically sealed, and scanned from 20 to 200 °C for GM and 20–250 °C for GMD and GMP at a heating rate of 10 °C/min under nitrogen (40 mL N_2/min). The instrument was calibrated with an indium metallic standard, and an empty pan was used as a reference. The measured parameters were calculated from the thermograms with Pirys software (PerkinElmer de México, S. A.).

3. Results and discussion

3.1. Extraction and characterization of galactomannans from Prosopis velutina

3.1.1. Galactomannan extraction process

The yield of GM extracted from the mesquite seeds of *P. velutina* was 11.12 %. This yield was lower than those reported by López-Franco et al. [5] (14.2 %) and by Bouttier-Figueroa et al. [22] (17 %) for mesquite GM of the genus *Prosopis* spp. And by Martínez-Ávila et al. [23] (16.53 %) for *P. glandulosa*. In contrast, our result was higher than that reported by Cunha et al. [24] for *P. juliflora,* 6.6 %. The differences in the extraction yields could be related to the culture conditions as well as other biological factors of the species, the origins of the seeds or the stage of development of the endosperm [25]. The extraction process used could be another factor, due to the nature of the extraction medium, the conditions under which extraction was carried out (temperature and pressure), the components of the seeds used determine the interaction of the GM with the medium and the variations in the extraction yields [26]. For example, acidic extraction tends to result in a lower molecular weight of GM or even a decrease in galactose branching [1]. There are many factors, both source physiological factors, handling and storage, as well as extraction conditions, that result in the inherent polydispersity of polysaccharides such as GM.

3.1.2. SEC-MALLS analyses

Table 1 shows the macromolecular characteristics of GM determined with SEC-MALLS. The Mw and intrinsic viscosity (Ƞ) were 4.44×10^5 Da and 2.68 dL/g, respectively. It is important to emphasize that these physicochemical parameters were influenced by both the extraction method and the endosperm development stage [27,28].

3.1.3. Compositional analyses

The GM from *P. velutina* showed a moisture content of 4.9 %, a low total fat content of 0.17 %, and a protein content of 1.0 % (Table 2). This composition was due to the aqueous extraction and purification processes to which the GM was subjected. In contrast, the ash content was high (5.6 %) compared to previous reports of other species of *Prosopis,* 1.8 % in *P. glandulosa* [23] and 3.6 % in *Prosopis* spp. [22], which indicated a higher content of inorganic matter present in the extracted polysaccharide. However, the major component of the GM was the total carbohydrate content of 94.5 %, which was similar to those reported by different authors, e.g., 99 % in *Prosopis* spp [5]. and 96 % in *P. glandulosa* [23]. These results confirm the importance of the extraction method, since with the aqueous method we were able to obtain a high amount of total carbohydrates of interest, as well as the compositional differences inherent to the source.

3.1.4. Solubility

The GM solubilities (Fig. 2) at different concentrations (0.5 and 1.0 % w/v) and temperatures (25 and 40 °C) were evaluated with water and DMSO solutions. A clear solvent effect was observed, and the GM was less soluble in DMSO than in water; in this case, dispersed small particles were observed, probably because the polysaccharide was not able to form H^+ bridges with DMSO, which prevented dissolution. In addition, a temperature effect was observed when DMSO was used. In contrast, GM was highly soluble (>90 %) in water with no effect of concentration or temperature. Similar behavior was reported by Liu et al. [29] for *Sesbania cannabina* and by López-Franco et al. [5] for *Prosopis* spp., with solubility percentages of 80–92 %. These solubility properties of GM may be associated with the M/G ratio because it has been reported that with more galactose branching, the polysaccharides exhibited higher solubilities [30]. Finally, the solubility of GM is only in polar protic solvents due to its high capacity to form H+ bridges; polar aprotic solvents such as DMSO do not allow its complete solubilization but its dispersion. This capacity is of crucial importance in the synthetic route proposed in our objectives to obtain GM esters.

Table 1
Macromolecular characteristics of mesquite galactomannan (*P. velutina)* from Baviacora (Sonora, Mexico).

	Mean ± SD
Weight-average molar mass (Mw) (Da)	$4.44 \times 10^5 \pm 2.3$ %
Number-average molar mass (Mn) (Da)	$1.79 \times 10^5 \pm 12.5$ %
Polydispersity index (PDI = Mw/Mn)	2.5 ± 0.3
Intrinsic viscosity [Ƞ] (dL/g)	2.68 ± 0.01

Data are means (n = 3) ± standard deviation.

Table 2
Compositional analysis of mesquite galactomannan (*P. velutina*) from Baviacora (Sonora, Mexico).

Component (%)	Mean ± SD
Moisture	4.9 ± 0.2
Total carbohydrates[a]	94.5 ± 5.4
Ashes[a]	5.6 ± 1.1
Total fat[a]	0.17 ± 0.04
Total protein[a]	1.00 ± 0.06

Data are means (n = 3) ± standard deviation.
[a] All measurements are on a dry weight basis except for moisture.

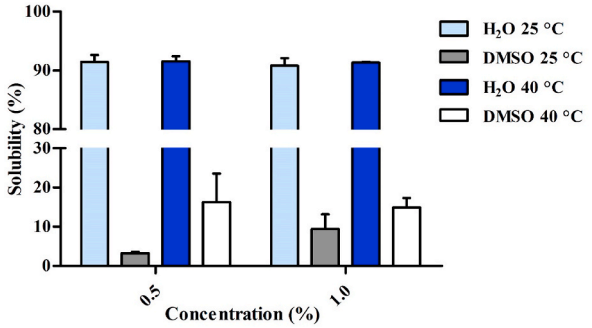

Fig. 2. Solubility of mesquite galactomannan from *P. velutina* in water and DMSO at 25° and 40 °C at concentrations of 0.5 and 1.0 % w/v.

3.1.5. ^{1}H NMR spectroscopy

The M/G ratio were determined by ^{1}H NMR from the relative areas of the signals for the anomeric protons (Fig. 3). The signals corresponding to the anomeric proton H^{+} of α-galactopyranose and β-mannopyranose appeared at δ 5.07 and 4.8, respectively, as reported by Cunha et al. [18]. The M/G value obtained was 1.2, this result is lower than that reported by Lopez-Franco et al. [5] (M/G: 1.5) and Bouttier-Figueroa et al. [22] (M/G: 2.05) in *Prosopis* spp. in both cases, and by Martinez-Avila et al. [23] (M/G: 2.0) in *P. glandulosa*. Certainly, a high content of galactose branching in GM is directly related to its percentage solubility as mentioned above [30]. In this study, the M/G ratio was used as a base to determine the FA and the different molar proportions of the GM esters.

3.2. Transesterification and characterization of galactomannan esters

3.2.1. FTIR spectroscopy

Fig. 4 shows the spectrum of *P. velutina* GM, which was similar to that previously reported for this polysaccharide [5]. Stretching vibrations generating peaks in the 3500-3000 cm^{-1} range were attributed to the O–H bonds of the carbohydrate hydroxyl groups [22]. Likewise, the band at 2915 cm^{-1} was assigned to stretching vibrations of the C–H bonds, while the bands at 1200–950 cm^{-1} resulted from vibrational modes of the C–O–H bonds [4]. The combined stretching modes of these two signals observed at 2915 cm^{-1} and 1200–950 cm^{-1} indicated the presence of C–O–C bonds, which is a characteristic of the hemiacetals formed via monosaccharide

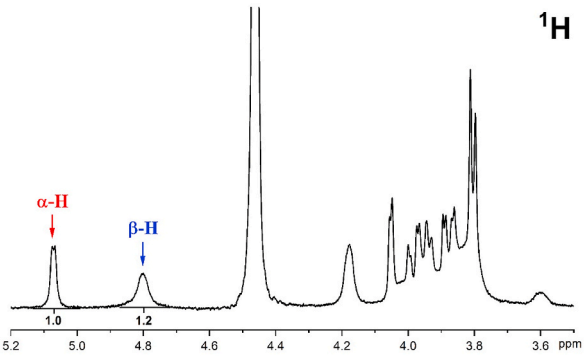

Fig. 3. ^{1}H NMR spectra of mesquite galactomannan from *P. velutina* in D_2O. The M/G ratio was determined according to the relative areas of the signals corresponding to the anomeric proton H+ of α-galactopyranose (δ 5.07) and β-mannopyranose δ 4.8), respectively.

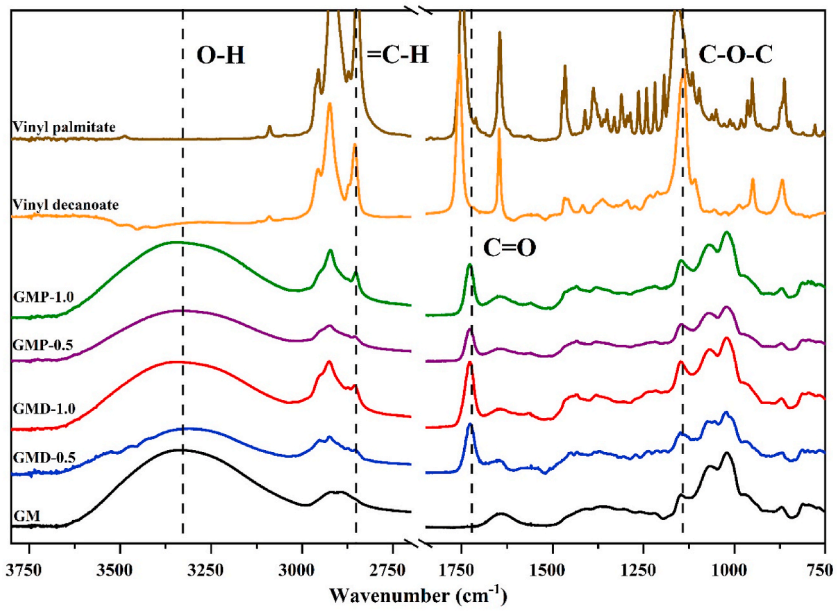

Fig. 4. FTIR spectroscopy of vinyl esters used as acyl donors, GMD-05, GMD-1.0, GMP-05 and GMP-1.0 synthesized by enzymatic transesterification in DMSO, and GM from *P. velutina*.

cyclization and of the glycosidic bonds characteristic of polysaccharides [6]. On the other hand, the bands at 870 and 815 cm^{-1} have been associated with the anomeric configurations of the β-D-mannopyranose and α-D-galactopyranose units, respectively [24]. The stretching peak at 1650 cm^{-1} corresponded to the amide functional groups, which have been associated with proteins. However, this band was associated with bending vibrations of the O–H bonds in water adsorbed by the sample [31]. On the other hand, the spectra for the GM esters (GMD and GMP at molar ratios of 0.5 and 1.0) showed bands at 1730-1750 cm^{-1} corresponding to C═O bond stretching vibrations, thus confirming the presence of esters [12]. This was supported by the 1150 cm^{-1} band corresponding to the carbonyl C–O–C bonds. Finally, for GMD-0.5 and GMP-0.5, the 2855 cm^{-1} band corresponding to the C–H bonds of sp_2 carbons disappeared, indicating depletion of the vinyl AG (decanoate and palmitate); for GMD-1.0 and GMP-1.0, there was a small shoulder, which could be due to small impurities even from the acyl donor [20].

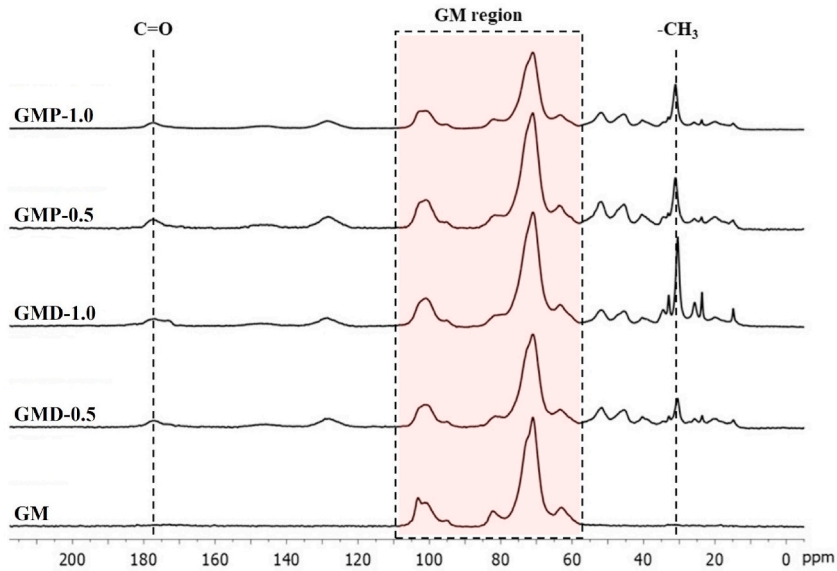

Fig. 5. CP/MAS ^{13}C NMR spectrum of GM from *P. velutina* and, GMD and GMP esters synthesized by enzymatic transesterification in DMSO spun at 10 kHz to determinate its esterification and DE.

3.2.2. ^{13}C-CP/MAS NMR spectroscopy

Successful esterification of the GM samples was confirmed with CP/MAS ^{13}C NMR spectroscopy. The spectrum of GM showed (Fig. 5) peaks for C1 at approximately 103.1 (Man) and 100.7 ppm (Gal). The region between 62 and 82 ppm contained strong signals, which were assigned to various ring carbons of the mannose backbone as well as the galactose side chains. C4, C5, and C6 of the branched mannose unit overlapped at 82.2 ppm. The signal at 62.8 ppm was due to C6 (Man and Gal) [18]. Evidently, in the spectra of GM ester derivatives (GMD and GMP with molar ratios of 0.5 and 1.0), the presence of two signals at 30.4–31.0 ppm and 176.0–177.8 ppm was characteristic of the terminal methyl groups of the aliphatic chains and carbonyl (C═O) groups, respectively, which confirmed the presence of FA ester in the C6 of galactose in modified GM [20,32]. In this sense, we can confirm the regioselectivity for the positions to primary alcohols described above for the use of enzymatic catalysis, because it prioritizes the esterification that require less energy (primary alcohols) with respect to more energy (secondary and tertiary alcohols) [13].

Table 3 shows the DE for GMD-0.5 (0.37), GMD-1.0 (0.71), GMP-0.5 (0.47), and GMP-1.0 (0.57), which were consistent with the molar ratios used in their synthesis and had a high content of different esterified FA. It has been previously described that the enzymatic catalytic activity of Lipase B from *C. antarctica* under aqueous (polar protic) conditions tends to promote hydrolysis more than the esterification process [14]. In contrast, it has been previously reported that the use of DMSO, as in our study, or DMF (aprotic polar solvents) decreases the formation of H^+ bridges, leading to increased enzyme activity and thus DE [15–17]. However, as a limitation of our work, is that despite having high DE and the regioselectivity of esterification, our reaction at 48 h does not achieve 100 % esterification efficiency of the molar ratios used. In this sense, further studies are needed to standardize the process for a better control of the DE in the synthesis of GM esters.

3.2.3. Thermal properties

The GM and derivatized GM ester samples were analyzed by DSC to understand the thermal transitions and how they were influenced by the polysaccharide structure, and the results obtained are included in Table 3. The GM, GMD and GMP exhibited similar thermal properties since they had similar glass transition temperatures (Tg) within the range 43–51 °C, which were similar to that reported for GM from the genus *Prosopis* spp. (49 °C) [22], and the melting temperatures (Tm) remained the same for GMD and GMP with all molar ratios relative to GM. It was reported this could be related to the chemical structure of the derivatized polymer and included the Mw, the M/G ratio, and distribution, and particularly in this study, the degree of esterification and lengths of the esterified aliphatic chains [6,33]. This study is of particular importance since it could define future applications for different galactomannan esters based on the structural characteristics provided by transesterification of the polymers.

4. Conclusion

Enzymatic catalysis in polar aprotic media of GM esters provides new tools for synthetic routes with greater control in terms of reaction efficiency and a reduction in the generation of corrosive residues by conventional routes. In the present work, GM esters with different molar ratios and FA chain lengths were synthesized from GM isolated from the seeds of mesquite *P. velutina*. Enzyme was used to catalyze a displacement of the reaction towards its inverse function and provide regioselectivity in the process of esterification, the correct synthesis was confirmed by the CP/MAS ^{13}C NMR and FTIR spectra. The thermal properties of the galactomannan esters measured by DSC were not modified by the synthesis process. These characteristics can be considered as a starting point for a more detailed standardization of the synthesis of galactomannan esters by enzymatic catalysis in polar aprotic media for future applications involving encapsulation or stabilization of systems with different hydrophobic components due to their amphiphilic characteristics.

Funding

The author, Gabriel H. Gómez-Rodríguez, acknowledges the Ph. D. scholarship (CVU No. 937367) provided by the Consejo Nacional de Humanidades, Ciencias y Tecnologías (CONAHCyT-México). We are grateful to the Laboratorio Nacional de Caracterización de Propiedades Fisicoquímicas y Estructura Molecular (UG-CONAHCyT–México) (Project: 123732) for ^{13}C-CP/MAS NMR and ^{1}H NMR spectroscopy analyses.

Ethical approval

Not applicable.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Gabriel H. Gómez-Rodríguez: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Gerardo González-García:** Writing – review & editing, Visualization, Validation, Investigation, Data curation. **Osiris Álvarez-Bajo:** Writing – review & editing, Visualization, Validation, Investigation. **Celia O. García-Sifuentes:** Writing – review & editing, Visualization, Validation, Investigation, Data curation. **Waldo M. Argüelles-Monal:**

Table 3
Degree esterification and thermal properties of galactomannan and galactomannan esters.

	DE	Tg (°C)	Tm (°C)
GM	–	51.21 ± 2.40	59.30 ± 0.16
GMD-0.5	0.37	48.24 ± 3.02	59.19 ± 0.02
GMD-1.0	0.71	51.10 ± 1.05	59.27 ± 0.35
GMP-0.5	0.47	51.27 ± 7.46	59.27 ± 0.31
GMP-1.0	0.57	43.52 ± 0.02	59.19 ± 0.22

Data are means (n = 2) ± standard deviation.

Writing – review & editing, Visualization, Validation, Investigation. **Jaime Lizardi-Mendoza:** Writing – review & editing, Visualization, Validation, Investigation. **Yolanda L. López-Franco:** Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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