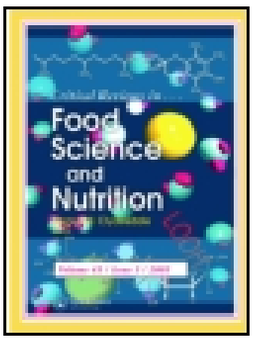

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REVIEW

A comprehensive review on leguminous galactomannans: structural analysis, functional properties, biosynthesis process and industrial applications

Priya Sharma, Sandhya Sharma, G. Ramakrishna, Harsha Srivastava, and Kishor Gaikwad

National Institute for Plant Biotechnology, ICAR, New Delhi, India

ABSTRACT

Galactomannans are neutral hemicellulose biopolymers that strengthen the plant cell walls by interacting with cellulose in the form of storage polysaccharides. They are abundant in nature and are majorly present in the secondary walls of flowering plants. They are primarily extracted from the leguminous seed endosperms and display a wide variation at the structural and abundance level amongst different plant species. Over the last few decades, galactomannans have attracted huge attention due to their unique functional, solution and rheological properties, generally defined by their molar mass and the degree of substitution by galactosyl side chain, which differs between plants. Further, they are nontoxic, originate from renewable sources, fairly inexpensive, and are amenable to both chemical and biochemical modification. Moreover, excellent thickening, stabilizing and gelling abilities of these biopolymers have found extensive use in food, pharmaceutical, biomedical and cosmetic industries. Significant progress has been made to identify and characterize the genes responsible for biosynthesis of galactomannan along with the elucidation of controlling networks by using genetic, bioinformatics and biochemical approaches. This is the first comprehensive coverage on galactomannans which combines detailed structural and physicochemical properties as well as biology associated with the metabolism of galactomannans. It also focuses on different leguminous sources leading to various food and non-food applications of galactomannans.

KEYWORDS

Galactomannan; polysaccharide; biosynthesis; properties; gum; M/G ratio; guar; fenugreek

Introduction

Plant cell wall is composed of various polysaccharides. These include cellulose, hemicelluloses and pectin. Among these, cellulose constitutes 30–50% of the cell wall total dry mass, while hemicelluloses makeup to 20–35% (Pauly and Keegstra 2008; Wang et al. 2012). On the basis of their backbone structure, hemicelluloses have been further grouped into mannans, xyloglucan and xylans (Wang et al. 2012). Mannan polysaccharides are pervasive in the cell walls of Charophytes (Popper and Fry 2003), and are subclassified into glucomannans, galactoglucomannans, mannans and galactomannans (Scheller and Ulvskov 2010). Mannans contain a linear backbone structure of β-(1→4)-linked repeating mannose units while backbone of glucomannans comprises of both mannose and glucose in a non-repeating pattern. Units of galactomannans and galactoglucomannans composed of β-(1→4)-linked mannose or mannose and glucose repeating units with a single unit of galactose side chain linked via α-1,6-glycosidic linkage at various intervals along the linear structural arrangement (Scheller and Ulvskov 2010). Glucomannans and galactoglucomannans are widely distributed in the secondary walls of the gymnosperms (Ebringerová, Hromádková, and Heinze 2005) and galactomannans are found to be deposited in the thickened secondary cell walls in angiosperm families like Leguminosae, Convolvulaceae, Annonaceae, Ebenaceae, Loganiaceae (Matheson 1990), Arecaceae/Palmae (Pettolino et al. 2001) and Rubiaceae (Sutherland et al. 2004).

The solutions and dispersions of galactomannan are mucilaginous, hence can also be known as seed mucilages or gums (Meier and Reid 1982). Gums are divided into three main categories: (a) Natural gums- naturally produced in plants, (b) Modified natural gums- manufactured by the chemical modification of natural gums or gum like material, (c) Synthetic gums- totally synthesized by chemical synthesis (Sharman, 1974). The seed gums are the reserves of carbohydrates in the endosperm walls of seeds as opposed to storage cotyledons (Reid 1985) and is speculated that they may provide mechanical support and control the emergence of the radicle too (Buckeridge 2010). Based on the occurrence and composition of endosperm mucilages, seeds of different plants vary in their galactomannan content (Anderson 1949). During early 1948, Whistler briefly worked on clusterbean (*Cyamopsis tetragonoloba*) and characterized the molecular and structural properties associated with the pure form of galactomannan. Drought tolerance of guar has been observed to depend on galactomannan which has the ability to imbibe large amounts of water and this could be the reason for its adaptive nature in the arid regions of India. This property of guar has also directed its use as drought tolerant

CONTACT Kishor Gaikwad kish2012@nrcpb.org National Institute for Plant Biotechnology, LBS Centre, Pusa Campus, New Delhi, Delhi 110012, India.

model system (Reid and Bewley 1979). Post these findings, production of guar gum has increased rapidly because of its cost-effectiveness, versatility and industrially attractive properties (Mudgil, Barak, and Khatkar 2014).

Galactomannans form the basis for their food and non-food uses due to their unique functional properties (like hydrophilicity, regulation of rheological behavior, adjustment in freezing and evaporation rate, alteration in ice-crystallization, emulsifying tendency, etc.), chemical-free nature (Gupta and Variyar 2018), and variation in Mannose/Galactose (M/G) ratio (Srivastava and Kapoor 2005). Industrially important legumes in terms of galactomannan production include carob bean (*Ceratonia siliqua*), guar (*Cyamopsis tetragonoloba*), fenugreek (*Trigonella foenum graecum*), tara (*Caesalpinia spinosa*) and senna (*Senna occidentalis*). Besides, some non-legumes like coffee, coconut, oil palm, date palm and nut palm are also rich sources of galactomannan gums. In this review, we have discussed in detail the biochemical backbone structure, physicochemical properties, biosynthetic mechanism of galactomannan and genetic regulation process in a wider context. Furthermore, different extraction processes and applications of galactomannan derived from major leguminous sources are also reviewed.

Structural composition of galactomannan

The determination of galactomannan chemical structure has been the subject of great interest and several experiments have been carried out to study the detailed structure of galactomannan from different plant sources. First attempt was made by Nadelman in 1890. He studied the developing seeds of *Trigonella foenum-graecum, Tetragonolobus purpureus, Colutea brevialata,* and *Indigofera hirsuta* and discovered the deposition of mucilages (or galactomannan) as secondary membrane thickenings of the endosperm cell walls (Meier and Reid 1982). With the development of sophisticated techniques, researchers have been able to identify the structure of galactomannan by chemical, biological and physical means. Chemical methods involve acid hydrolysis with subsequent identification of the components by their osazones, or by paper chromatography, periodate oxidation, methylation and subsequent hydrolysis and by developing sulfonyl derivatives (Chudzikowski 1971). Biological methods include selective enzyme hydrolysis and physical methods include study of optical rotation, infrared spectroscopy, stress-strain measurement, X-ray analysis of films of pure gum and its acetate and NMR.

Main covalent backbone

Smith (1948) had studied the structure of carob gum by means of methylation of gum directly or by first converting it into its acetate form followed by methylation. He reported that the gum obtained from carob bean consisted of 80% D-mannose and 20% D-galactose. Subsequently, Hirst and Jones (1948) also arrived at the same result for carob seed gum by means of methylation and periodate oxidation. They isolated three different types of sugar derivatives from carob gum: 2,3,4,6-tetramethyl-D-galactose, 2,3-dimethyl-D-mannose and 2,3,6-trimethyl-D-mannose upon complete hydrolysis whereas Whistler and Stein (1951) isolated two disaccharides 4-β-D-mannopyranosyl-D-mannose and 6-α-D-galactopyranosyl-D-mannose from guar gum upon partial hydrolysis. The D-mannopyranose residues was found to be linked via β-1,4 glycosidic bonds and produced 2,3,6-trimethyl-D-mannose upon methanolysis while 2,3,4,6-tetramethyl-D-galactose formed from units of galactose present at the branch points and 2,3-dimethyl-D-mannose were produced from the main backbone chain of mannose to which the galactopyranose side chains are attached via 1,6-glycosidic linkages (Smith 1948). It was also concluded that galactomannan from guar seed contains 1,4 linkages in the D-mannopyranose backbone (Moe, Miller, and Iwen 1947). The presence of α- 1, 6 linkages in between the D-galactosyl stub and main D-mannan backbone (i.e., at branching points) was first suggested in carob gum and confirmed in guar gum by measuring the change in the optical rotation upon acid hydrolysis (Heyne and Whistler 1948) and the results were subsequently supported by X-ray diffraction studies (Palmer and Ballantyne 1950). A representation of general structure of galactomannan is depicted in Figure 1.

The structure of other plant-seed gums were examined by the same techniques and it was found that most of them have the same fundamental structure while the degree of substitution by D-galactosyl side groups varies widely. Plants reported to have the galactomannans of this type include *Gleditsia triacanthos*, *Gleditsia amorphoides*, *Cassia fistula*, *Cassia nodosa*, *Cassia occidentalis*, *Cassia tora*, *Lotus pedunculatus*, *Lotus corniculatus*, *Trigonella foenum-graecum*, *Medicago lupulina*, *Medicago sativa*, *Desmodium pulchellum* and *Anthyllis vulneraria* (Leguminosae family); *Arenga saccharifera*, *Borassus flabellifer* and *Cocos nucifera* (Palmae family); *Annona muricata* (Annonaceae family); *Ipomoea muricata* and *Convolvulus tricolor* (Convolvulaceae family) (Dea and Morrison 1975).

Nonetheless, galactomannans of some seeds have evolved to diverge from the basic structural pattern, differing mainly in the D-mannan backbone and the branching pattern (Kapoor and Mukherjee 1969, 1971; Unrau and Choy 1970), although this divergence has not been observed to affect their physical and chemical properties.

Fine structure prediction with side chain analysis

Different methods like enzymatic hydrolysis of guar gum (Mccleary 1979), computer simulation methods (McCleary et al. 1985) and spectroscopic techniques (Grasdalen and Painter 1980) revealed random structural allocation of α-D-galactose side chains along the mannan backbone rather than the regular distribution as presumed earlier (Whistler and Hymowitz 1979).

The relative content of D-galactose substituted along the mannan backbone has also been determined at the genetic level. The ratio of mannose to galactose in galactomannan isolated from carob, honey locust and guar was found to be

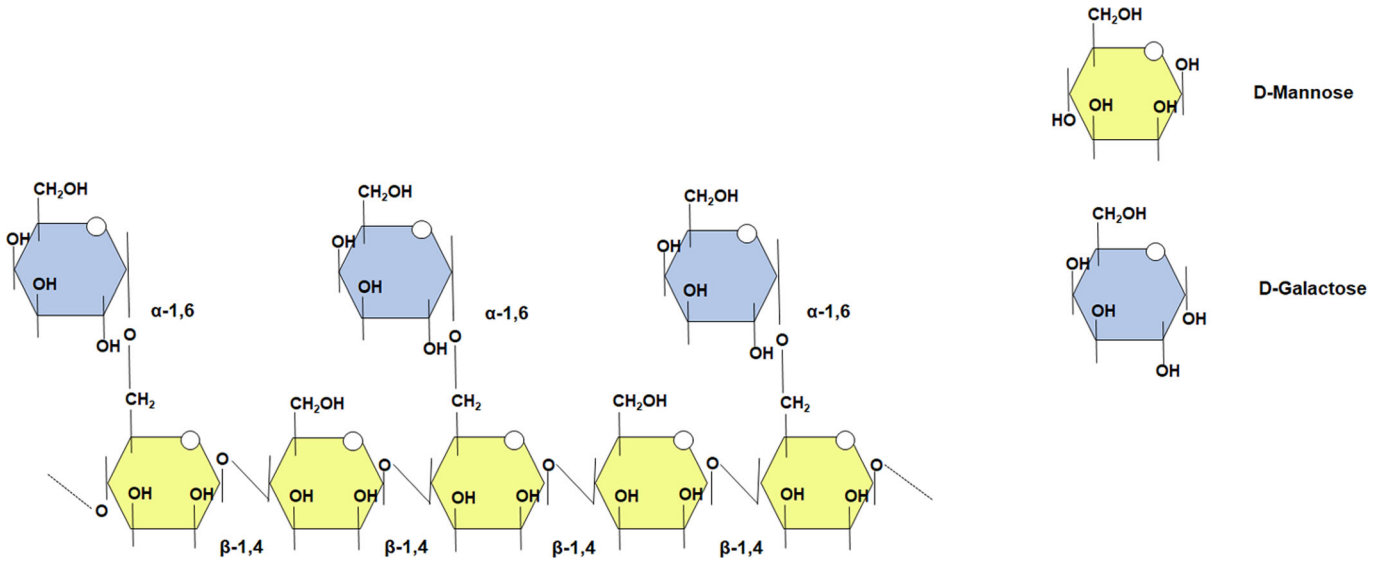

Figure 1. General structure of galactomannan.

3.0–4.0:1, 4.4:1, and 2:1, respectively (Moe, Miller, and Iwen 1947). X-ray diffraction analysis indicated that the side chains consist of single galactopyranoside unit on every second mannose residue in guar galactomannan (Palmer and Ballantyne 1950). To study the structural changes in galactomannan, purified β-mannnases were used to degrade legume seed galactomannans (Mccleary and Matheson 1975; Mccleary 1979). NMR studies performed by Grasdalen and Painter (1980) were found to be in agreement with the above results obtained by chemical analysis.

Fenugreek gum has a molar ratio of 1:1 (D-mannose to D-galactose) as it has the largest proportion of galactose in comparison to carob and guar gum. Muschin and Yoshida (2012) performed the structural analysis of four gums (guar gum, carob bean gum, fenugreek gum and tara gum) by using high resolution NMR spectroscopy and reported for the first time that only fenugreek gum contained more than two galactopyranosidic side chains linked with the α-1,4 linkage and are connected at O-6 with the main chain of D-mannan backbone.

Determination of absolute molecular weight of galactomannans has been technically difficult because of the highly viscous nature of galactomannan solution. Due to this, average molecular weight can be obtained and the value varies depending upon the techniques used viz, light-scattering methods, intrinsic viscosity measurements, sedimentation velocity, chemical methods and osmometry. The average molecular weights reported for a number of galactomannans are given in Table 1.

Global production of guar galactomannan

India stands at top in the world's guar gum production. It is cultivated mostly in north-western India with Rajasthan accounting for more than 78–80% of the area under guar production followed by Haryana (17%), Gujarat (4%) and Punjab (1%).

Due to increasing demand, the gum producing industry has seen reasonable increases in revenues and generated employment opportunities. Out of the total world production of 6.8–9.07 Lakh metric tonnes/year, India accounts for more than 75–82%. The increasing consumption has been driven by high demands from major petroleum players in the USA and Mideast. Major importers of guar gum include Canada, USA, UK, China, Russia and South American countries like Brazil, Chile and European nations like Germany, Greece, Italy, Portugal, Sweden and Netherland (NRAA 2014).

Physicochemical properties of galactomannan

Galactomannans are believed to exist in random coil conformation in aqueous solutions and more-ordered form, only under conditions which are favorable for aggregation or interaction with other species (Srivastava and Kapoor 2005). The presence of cis-OH groups in mannose enables the formation of hydrogen bond within the molecules of polymannan chain as long as substitution group like galactose is not present or less in amount (similar to carob bean gum). An increase in substitution by galactose side chain (alike guar gum) establishes steric hindrance between the molecules so that very less hydrogen bonding occurs and leads to high water solubility and causes significant changes in the viscosity of galactomannan (Prajapati et al. 2013). Thus, galactomannans can disperse easily in water and form strong hydrogen bonds on interaction with water molecules and hence, represents high water binding capacity (Gadkari et al. 2018). The fine structure of galactomannans including M/G ratio, positioning and orientation of galactose side groups along the mannan backbone, may greatly affect the polymer conformation and significantly affect its solution properties like solubility, viscosity and interaction with other polysaccharides to form gels (Wu et al. 2012). The rate of dissolution of galactomannan and viscosity development also depends on the physical parameters like structure of the

Table 1. Average molecular weight of different galactomannans (modified from Dea and Morrison 1975).

Species	Molecular weight (Da)	Method
Annona muricata	8,700	chemical
Arenga saccharifera	17,000	chemical
Borassus flabellifer	139,000	light scattering
Cocos nucifera	7,200	chemical
Convolvulus tricolor	11,000	chemical
Ceratonia siliqua	300,000	chemical
	150,000 (cold-water dissolvable fraction)	chemical
	650,000 (hot-water dissolvable fraction)	chemical
	310,000	sedimentation analysis
	1,198,667	HPSEC (High pressure size exclusion chromatography) (Brummer, Cui, and Wang 2003)
Cassia pulcherrima	60,000	sedimentation analysis
Caesalpinia spinosa	1,000,000	light scattering (Santos et al. 2019)
Cyamopsis tetragonoloba	250,000	chemical
	1,900,000	sedimentation analysis
	1,720,000	light scattering
	950,000	osmometry, viscosity and light scattering
	1,000,000- 2,000,000	chromatography and laser light scattering (Mudgil, Barak, and Khatkar 2014)
	1,303,607	HPSEC (Brummer, Cui, and Wang 2003)
Trigonella foenum graecum	1,418,000	HPSEC (Brummer, Cui, and Wang 2003)

galactomannan, pH, temperature and salt concentration (Maier et al. 1993).

Rheology

Rheology can be described as the science used to study the stresses generated during mechanical stress and flow behavior of non-Newtonian fluids. Rheological properties (viscosity, intrinsic viscosity, viscoelasticity and entanglement behavior) needs to be investigated in order to validate the usefulness of any polymer for food and non-food applications (Gadkari et al. 2018).

The concentration of polymer has a wide impact on the solution rheology and hence requires thorough knowledge for both product and process design (Torres, Hallmark, and Wilson 2014). With the increase in concentration of polymer, transition into semi-dilute from dilute state takes place at a certain concentration called as critical concentration (C^*) and volume occupancy by the isolated polymer coil appears to decrease at this concentration. At concentrations above C^* (>0.1%), the polymer coils starts compressing through the overlapping of the macromolecular chains and give rise to 'entanglements' (Gillet et al. 2017). These entanglements are formed due to self-association of unsubstituted regions of mannan backbone (Doyle, Lyons, and Morris 2009). The presence of these entanglements affect the flow behavior of polymers and higher viscosities were observed for concentrations above C^* (Sittikijyothin, Torres, and Gonçalves 2005). Hence, the flow behavior of polymer solutions is majorly affected by the molecular weight and concentration of the polymer (George and Qureshi 2013).

Galactomannan and other polymers (both natural and man-made) with large molecular weight don't obey Newton's law of viscosity. Instead, they show shear thinning or pseudoplastic behavior, i.e., their viscosity declines with increasing shear rate, and hence variously known as rheologically complex, non-linear or non-Newtonian solutions (Chhabra 2010). These type of polymers also exhibited Newtonian behavior at very low shear rates (Chhabra and Richardson 2008) because the rate of formation of disentanglements was fairly balanced by the reorganization of new entanglements at very low shear rate and display constant viscosity. But at high shear rate, forced disentanglements predominates over the reorganization of new entanglements by which individual polymer chains gets the freedom of movement and aligned in the flow's direction and leads to lowering of viscosity (Sittikijyothin, Torres, and Gonçalves 2005). The degree of non-Newtonian behavior owned by any polymer depends on the various factors like polymer size, electrostatic charges on the polymer, shape and distribution of polymer particles, and steric effects (George and Qureshi 2013).

Galactomannans are also categorized as visco-elastic fluids because they show features of both ideal elastic solids and fluids and exhibit capability to store and recover shear energy. In simpler words, it can be understood by the 'soup bowl' effect. If soup in a bowl is made to rotate by means of spoon (the source of gentle stirring), the liquid soup will slowly come to a stop on removing the spoon and inertial circulation will disappear as a result of this action (Chhabra and Richardson 2008). Viscoelasticity arises from interactions between components in the fluids or gum solutions and has been studied by using the dynamic measurements (Robinson, Ross-Murphy, and Morris 1982; Sittikijyothin, Torres, and Gonçalves 2005; Shobha and Tharanathan 2009). G' (conservative/storage modulus) indicates the elasticity (solid-like behavior) while G'' (dissipative/loss modulus) provides information on the viscoelasticity (liquid-like behavior) of the material. It has been shown that several galactomannans (at high concentrations) possess liquid-like behavior ($G'' > G'$) at lower frequency of oscillation, while more like a solid ($G' > G''$) at higher frequencies. The random coil polymers obtained from different polysaccharides generally follow a similar rheological pattern formed from synthetic polymers but deviations do occur for guar and carob bean gum at high ionic strength and low pH due to presence of the hyperentanglements (Morris et al. 1981).

Rheological properties can be customized if high molecular weight galactomannan is converted into low molecular weight galactomannan (high M/G ratio) by debranching of galactose residues with suitable enzymes (Mahammad et al. 2007; Shobha and Tharanathan 2009).

Viscosity

A fluid's viscosity is a measure of its internal friction to flow. Newton's law of viscosity describes the interrelation between the shear stress and rate of shear of a fluid subjected to deformation, i.e., the ratio of stress to shear rate is a constant at fixed pressure and temperature and is defined as the dynamic viscosity (Chhabra 2010). Magnitude of viscosity depends on two principal factors, molecular weight and intrinsic chain stiffness of polymer molecules (Morris et al. 1981). The viscosity of Newtonian fluids is constant and doesn't depend on the shear rate whereas for non-Newtonian fluids, it depends on the shear rate. Hence, a single mode of assessment is insufficient to specify the flowability of the non-Newtonian fluids (George and Qureshi 2013).

The intrinsic viscosity is defined as a measure of the volume occupied by the discrete polymer molecules in solution and is directly dependent on the molecular mass (Richardson and Kasapis 1998). It also depends directly on radius of gyration and entanglement behavior (Doyle, Lyons, and Morris 2009) and dictates a rough estimate of molecular characteristics of the polymer and its interactions with the solvent molecules (Barak and Mudgil 2014). Aqueous dispersions of guar gum have been reported to have higher intrinsic viscosity compared to both carob gum and fenugreek gum (Gadkari et al. 2018). High solution viscosities of guar gum are attributed to its large volume and nature of its intermolecular association via hydrogen bonding (Cheng, Prud'homme, et al. 2002).

The presence of more galactosyl side groups in the galactomannan structure causes chain bending when kept in a solution and reduces the intrinsic stiffness of the chain (Mazeau and Rinaudo 2004) and also influences the gelation ability (Richardson et al. 1999). Among the major four gums, i.e., carob bean, guar, tara and fenugreek: carob bean gum was found to be the most stiffer one because of more unsubstituted mannan regions and exhibited a higher propensity to form gels as a result of synergism by forming "junction zones" (Wu et al. 2012). These junction zones are a type of intermolecular non-covalent interactions, formed between the galactomannan backbone and side chains of other biopolymer (Fernandes 1995). Tara and guar gum fall in the middle range and are able to form hyperentanglements due to presence of average unsubstituted mannan regions and also form solutions of higher viscosity than the other gums but fenugreek gum act as the most compact and flexible one and no large ordered structures (or entanglements) were obtained for it (Wu et al. 2012). Viscosity also depends on the method of solubilization, time, temperature, pH and ionic strength (Mudgil, Barak, and Khatkar 2014). It was reported that the viscosity of tara gum was reduced when salts ($CaCl_2$ and NaCl) were present and was able to maintain the constancy over a wide pH range (3–11) (Wu et al. 2015).

It has been suggested that gum solutions possess time-dependent change in viscosity known as thixotropy, which means that the magnitude of viscosity decreases with time at a constant shear rate (Marcotte, Hoshahili, and Ramaswamy 2001; Kök 2010). The viscosity of gum solutions was found to increase with the concentration, possibly due to an increase in water binding capacity as described earlier, thereby reducing the availability of free water and limiting the dispersion flow at higher concentrations (Gadkari et al. 2018). Table 2 summarize the rheological properties exhibited by major galactomannans.

Temperature

Temperature is a notable factor considered during processing of hydrocolloids because it strongly influences the flow behavior of gum solutions (Marcotte, Hoshahili, and Ramaswamy 2001). Generally, the viscosity of most liquids decreases with increase in temperature (Chhabra 2010) but increase in viscosity with rise in temperature has been noticed in gum solutions having high M/G ratio (Gaisford et al. 1986). It is reported that galactomannans with higher degree of galactose substitution (low M/G ratio) are soluble at room temperatures (25–30 °C) while unsubstituted content (high M/G ratio) needs heat treatment upto 90 °C for maximum solubility (Gaisford et al. 1986; Kök, Hill, and Mitchell 1999) and hence, the response of temperature on viscosity could vary with the source of hydrocolloid (Wu et al. 2015). The temperature range of 25–40 °C is best for achieving maximum viscosity for guar gum solutions but carob bean gum solution cannot disperse easily at room temperature and possess very low viscosity (Dea and Morrison 1975). In case of tara gum, increase in temperature from 20 °C to 80 °C causes reduction in the viscosity due to depolymerization of polymer molecules at high temperature (Wu et al. 2015). Crosslinking of guar gum with other materials like borates and metal ions, increases its resistance to degradation at high temperatures and effectively increases its viscosity (Maier et al. 1993).

pH

Due to nonionic and uncharged behavior, gum solutions was found to be consistent over a pH range of 1.0 to 10.5 (Srivastava and Kapoor 2005; Mudgil, Barak, and Khatkar 2014) but this is not true for all galactomannans. It has been shown that a change in pH value has a remarkable effect on the rheological parameters (Hosseini et al. 2017). The apparent viscosity reached upto maximum value at pH 7 and reduced at lower and higher pH values (Hosseini et al. 2017; Farahnaky et al. 2014). At acidic pH, less number of hydrogen bonds are formed between molecules of water and galactomannan causing reduction in viscosity (Farahnaky et al. 2014). At alkaline pH, hydroxyl groups of galactomannan become ionized, thus converting neutral polymers to polyelectrolytes that cause electrostatic repulsion (and repressed the

Table 2. Summary of rheological properties exhibited by major galactomannans.

S.No	Rheological properties	Guar gum	Carob bean gum	Fenugreek gum	Tara gum	References
1.	Viscosity (based on molecular mass)	Moderate	Low	High	Low	Wu et al. 2009; Gadkari et al. 2018
2.	Intrinsic viscosity	High	Low	Moderate	Low	Wu et al. 2009; Gadkari et al. 2018
3.	Entanglement behavior	High	Moderate	Very low	Low	Robinson, Ross-Murphy, and Morris 1982; Wu et al. 2012; Sittikijyothin, Torres, and Gonçalves 2005
4.	Flow behavior	Non-Newtonian				Maier et al. 1993
5.	Viscoelasticity	Liquid like form (G″> G′)				Robinson, Ross-Murphy, and Morris 1982; Sittikijyothin, Torres, and Gonçalves 2005; Wei et al. 2015; Wu et al. 2015
	I. At low frequency of oscillation					
	II. At high frequency of oscillation	Gel-like form ((G′> G″)				
6.	Chain stiffness	Moderate	High	Low	Moderate	Wu et al. 2012
7.	Gelation ability (At low concentration, <1%)	Weak gels	Strong gels	Weak gels	Weak gels	Maier et al. 1993; Wei et al. 2015
8.	Thixotrophy	No	Yes	Yes	No	Mao and Chen 2006; Wei et al. 2015; Wu et al. 2015

Note. Abbrevations: G′- conservative or storage modulus, G″- dissipative or loss modulus

formation of hyperentanglements) and therefore decrease dispersion viscosity (Doyle, Lyons, and Morris 2009). Goycoolea, Morris, and Gidley (1995) and Doyle, Lyons, and Morris (2009) studied the effect of neutral and alkaline pH on the viscosity of guar, carob bean and fenugreek gum and observed the same trend as described above in all three gum solutions. In contrast, a slightly different result was also obtained for guar gum in which no significant change in viscosity was observed on increasing pH (Gadkari et al. 2018)

Salt concentration

Gums used in food preparation mostly act as polyelectrolyte and reacts with salts present in food (Salehi, Kashaninejad, and Behshad 2014). These interactions can change the biological and rheological properties of gum solutions (Goycoolea, Morris, and Gidley 1995; Khouryieh et al. 2007; Doyle, Lyons, and Morris 2009; Wang et al. 2015; Hosseini et al. 2017). It has been observed that gum solutions exhibit higher viscosity under lower concentration of salt and declined under high shear stress with rising ionic strength (Hosseini et al. 2017). This decrease was observed due to electrostatic repulsion which leads to a close-packed conformation and reduces the hydrodynamic volume of polymer (Khouryieh et al. 2007; Hosseini et al. 2017; Gadkari et al. 2018). Gadkari et al. (2018) studied the effect of salt concentration with increasing pH (3–7) on three industrially important gums viz, guar, carob bean and fenugreek gum. They found that the apparent viscosity did not change significantly for guar and carob bean gum at constant salt concentration, but for fenugreek gum, a decrease in viscosity with increase in pH was observed. With the addition of NaCl in increasing concentration (0.1–1 M), the apparent viscosity of all three dispersions decreased.

Rate of hydration

The hydration or dissolution process of water-soluble galactomannans can be influenced by a number of factors, including particle size, molecular weight and final solution concentration (Wang, Ellis, and Ross-Murphy 2008). Hydration for a time span of two hours was recommended in order to attain maximum viscosity for practical implementation. Pulverized gum powder was shown to hydrate easily and more quickly than kibbled gum powder (Barak and Mudgil 2014). With increasing temperature and decreasing particle size and pH, the rate of dissolution of guar gum and viscosity generally rises while the hydration rate declines in the presence of water-dissolving agents such as salts and sucrose (Maier et al. 1993). It has also been shown that presence of excess salt (more than 1%) can slow down the hydration time. Thus, for maximum viscosity, gum hydration should be for extended time in the absence of salt (Gadkari et al. 2018).

Hydrogen bonding

Hydrogen bonding is one of the most important characteristic of galactomannans. Due to the presence of hydroxyl groups in its structure, galactomannans adsorb easily onto the hydrated cellulose fibers and mineral surfaces which make them very useful in paper and mining industry (Prajapati et al. 2013). Carboxymethylated gum shows magnificent hydrogen bonding effects by which lightweight papers can be manufactured with excellent tightness (Prajapati et al. 2013). Substitution of galactomannan hydroxyl groups with hydroxypropyl causes steric hindrance thereby causing a reduction in the stability of hydrogen bonds (Cheng, Prud'homme, et al. 2002).

Biosynthesis of galactomannan

Hemicellulosic/non-cellulosic polysaccharides including galactomannans are synthesized in the lumen of Golgi apparatus and are delivered to the surface of cell via secretory vesicles and incorporated into the wall matrix (Ray, Shininger, and Ray 1969). Galactomannan biosynthesis occurs via a complex pathway involving several reactions

and is closely connected to the central metabolism. Detailed biosynthetic process with the involvement of different genes has been explained in the following section.

Most of the carbon is transported as sucrose in plants because of its non-reducing nature. The α-1, 2-glycosidic bond present in sucrose can be cleaved irreversibly/reversibly by the action of Invertase/Sucrose synthase as depicted in Figure 2. Invertase catalyzes the splitting of sucrose into glucose and fructose, and sucrose synthase converts sucrose into UDP-glucose and fructose in the presence of UDP. Fructose is phosphorylated by fructose kinase to form fructose-6-phosphate and isomerizes into mannose-6-phosphate by Phosphomannoisomerase. Then, Phosphomannomutase transfer phosphate group from carbon 6 to carbon 1. Further, GDP-mannose pyrophosphorylase utilizes this mannose-1-phosphate and produce GDP-Mannose by removing the inorganic phosphate. Conversion of UDP-glucose into UDP-galactose is catalyzed by UDP-galactose 4-epimerase. Synthesis of substrates like GDP-mannose and UDP-galactose takes place in the cytoplasm and then transported into the Golgi by sugar nucleotide transporters for the galactomannan biosynthesis (Seifert 2004). Mannan synthase thus produces the mannan polysaccharide backbone by utilizing GDP-mannose and galactosyl residues are transferred from UDP-galactose to the mannan backbone by Galactosyltransferase and produces galactomannan (Figure 2) (Dhugga et al. 2004; Edwards et al. 1989). The standard M/G ratio can be varied *in vitro* by keeping the UDP-galactose levels at constant and altering the GDP-mannose concentration (Reid, Edwards, and Dea 1987). However, degree of substitution by galactose units in the mannan backbone is determined at the stage of biosynthesis and can be controlled either at the formation process or by the selective removal of galactosyl units during hydrolysis, by α-galactosidase (Edwards et al. 1992). This post-depositional process has been described in later section.

Genes involved in the biosynthesis of galactomannan

The first plant cellulose synthase was identified by random expressed sequence tag (EST) sequencing from the developing cotton fibers (Pear et al. 1996). It has been predicted that the carbohydrate donors present in the cell requires hundreds of enzymes for the synthesis of non-cellulosic matrix polysaccharides (Perrin, Wilkerson, and Keegstra 2001) but till date, few genes have been identified and characterized (Table 3). Because of the reactive nature and low abundance, these genes were hard to identify by the process of biochemical purification, but identification and characterization of candidate genes has been relatively successful via gene expression profiling in heterologous system (Sandhu, Randhawa, and Dhugga 2009).

Mannan synthase (*ManS*) belongs to cellulose synthase like (*Csl*) family of genes and is involved in the formation of polymannan chain linked via β-1,4-glycosidic bonds (Dhugga et al. 2004). *Csl* proteins are membrane bound and predicted to have five or six transmembrane domain (Richmond and Somerville 2000). It was shown that ManS from guar seed endosperm and transgenic soybean somatic embryos are able to utilize only GDP-mannose as substrate. By raising antibodies against the ManS protein, it was confirmed that the Golgi targeting information was present in the primary sequence of ManS protein and even retained in the functional form in transgenic cells (Dhugga et al. 2004). Liepman, Wilkerson, and Keegstra (2005) performed an investigation to analyze the functions of a group of *Csl* genes from rice (*Oryza sativa* L.) and *Arabidopsis* by expressing them in *Drosophila* Schneider 2 (S2) cells. They reported that the ManS enzymes were encoded by the three *Arabidopsis CslA* genes viz, *CslA*2, *CslA*7 and *CslA*9. The presence of *CslA*9 protein was confirmed in the Golgi lumen by using the confocal microscopy and then the topology of *CslA*9 was investigated by tagging with T7 epitope and expressing in *Pichia pastoris* (Davis et al. 2010). This analysis also proposed that some nucleotide sugar transporters are definitely present which transport GDP-Man and UDP-Gal from cytosol to Golgi lumen in order to be utilized as substrate in the formation of galactomannan. Wang et al. (2012) identified the two putative nucleotide sugar transporters in fenugreek (*NST1* and *NST2*) where, NST1 showed strong resemblance with *Arabidopsis* UDP-Galactose transporter *At*NST-KT and NST2 to *Arabidopsis* UDP-Gal transporter *At*UDPGalT1 and GDP-Man transporter *At*GONST5, but accurate functionality is not yet known. A new 'mannan synthesis related protein' (MSR or *DUF246*) was identified which might behave as a glycosyltransferase and is involved in the priming of mannan polymers or responsible for the glycosylation of ManS or ManS-interacting proteins to enhance activity or stability of the complex (Wang et al. 2013).

The role of galactomannan galactosyltransferase (GGT) in making galactomannan was first identified in fenugreek by radio TLC method. It catalyzes the addition of single galactose unit from substrate UDP-galactose to the linear mannan backbone (Edwards et al. 1989). Reportedly, the domain of ManS was predicted to be on the same side of the Golgi cisternae with the α-galactosyltransferase for the galactose substitution to occur simultaneously during the backbone synthesis (Dhugga et al. 2004). It was also reported that galactosyl residues were not transferred when the GDP-galactose was used as a substrate. The relative concentrations of the precursors UDP-galactose and GDP-mannose drive the amount of galactose substitution content in the main mannan backbone among different leguminous species (Edwards et al. 1992). The specificity of GGT plays a major role in controlling the substitution of D-galactosyl side chain in galactomannan biosynthesis and tend to modify the chemical properties of different polysaccharides (Reid et al. 1995). The putative *GGT* encodes a 51.282 KDa protein, with a single transmembrane α-helix alongside N-terminal and its functional characterization was confirmed by cloning the cDNA into the genome of *Pichia pastoris* under the control of promoter like AOX (alcohol oxidase) and the yeast α-secretion factor (Edwards et al. 1999).

In coffee (*Coffea arabica* and *Coffea canephora*), two putative *ManS* (*ManS1* and *ManS2*) and two *GGT* (*GGT1*

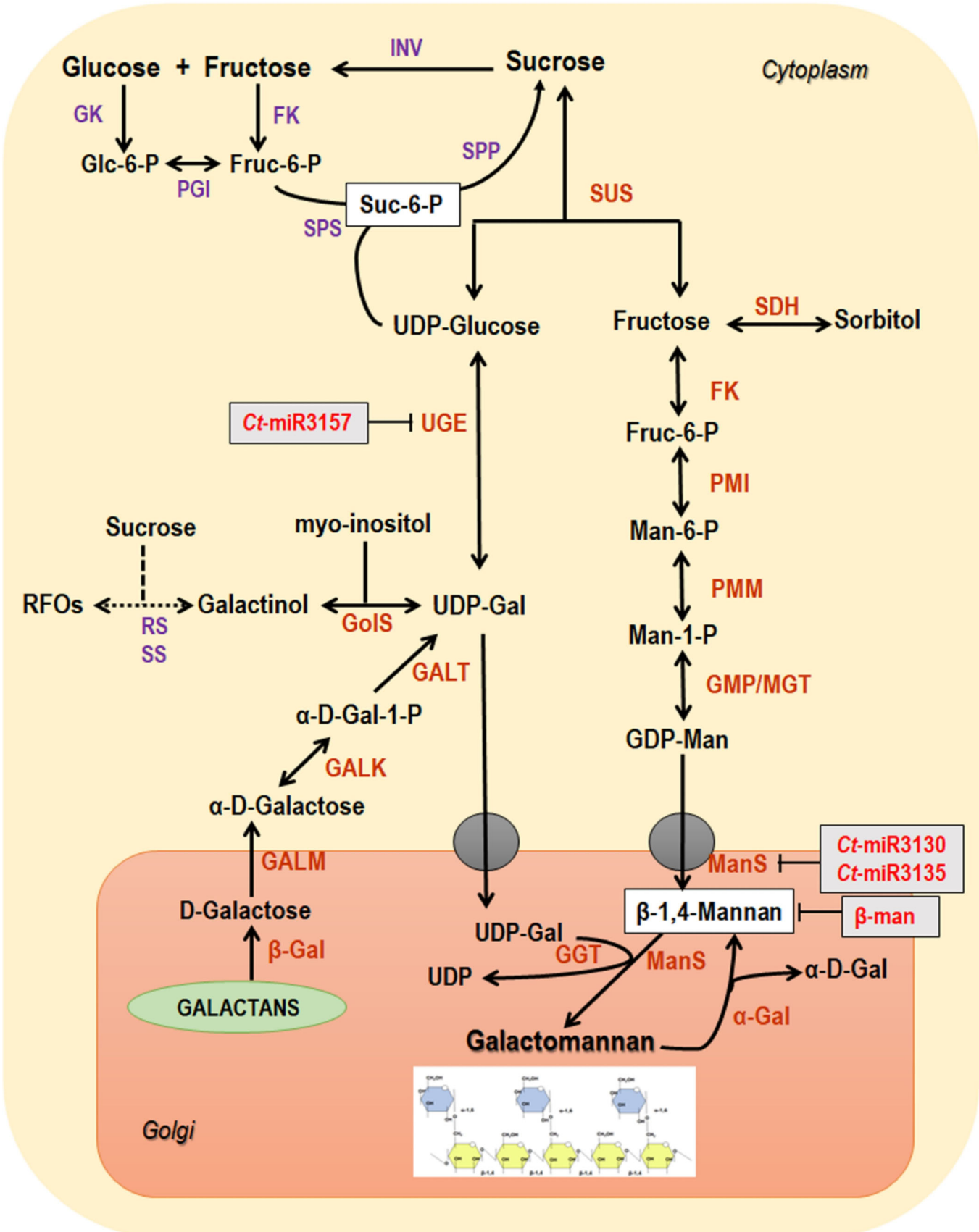

Figure 2. Biosynthesis of galactomannan and its control. Abbrevations: Glc-6-P, glucose-6-phosphate; Fru-6-P, fructose-6-phosphate; Gal, galactose; Man, mannose; SUS, sucrose synthase; UGE, UDP-glucose/UDP-galactose 4-epimerase; GMP/MGT, GDP-mannose pyrophosphorylase/mannose-1-phosphate guanyltransferase; FK, fructose kinase; GK, glucokinase; PMM, phosphomannomutase; PMI, phosphomannose isomerase; ManS, mannan sythase; GGT, galactomannan galactosyl transferase; GALM, aldose-1-epimerase; β-gal, β-galactosidase; α-Gal, α-galactosidase; β-man, β-mannosidase; RS, raffinose synthase; GALK, galactokinase; GolS, galactinol synthase; SS, stachyose synthase; SPS, sucrose phosphate synthase; SDH, sorbitol dehydrogenase; SPP, sucrose phosphate phosphatase; PGI, phosphoglucoisomerase; GALT, galactose-1-phosphate uridylyltransferase; INV, invertase; RFOs, raffinose family oligosaccharides.

Table 3. Genes involved in the biosynthesis of galactomannan.

Genes	Enzymes	Functions	Plant source for identification	References
ManS/ CslA (Cellulose synthase-like A)	Mannan synthase	Form mannan backbone via $\beta(1\rightarrow4)$ glycosidic activity	Guar	Dhugga et al. 2004; Liepman, Wilkerson, and Keegstra 2005
GGT	Galactomannan galactosyltransferase	Add galactose unit from UDP-galactose to linear mannan backbone via $\alpha(1\rightarrow6)$ glycosidic activity	Fenugreek	Edwards et al. 1989
MSR/ DUF246	Mannan synthesis-related	Unkown till date	Fenugreek	Wang et al. 2013

and *GGT2*) were reported for the galactomannan synthesis, out of which *ManS1* and GGT1 demonstrated to have the highest expression level during the development of endosperm in both *Coffea* species (Pré et al. 2008). The ManS or mannosyltransferases required divalent metal cations like, Mg^{2+}, Ca^{2+} or Mn^{2+} and GGT required specifically Mn^{2+} for their biological activity (Reid, Edwards, and Dea 1987).

Regulation of galactomannan biosynthesis

Much of the progress has been made to understand the core biosynthetic machinery for galactomannans, but their precise regulation is poorly understood as compared to other major secondary wall biosynthetic pathway like that of cellulose (Zhong et al. 2011). Galactomannan biosynthesis is very complex and coordinated process with several checkpoints. Various enzymes are reported to act synergistically in this pathway. Also, genes required to synthesize galactomannans must be tightly regulated at various stages of their expression due to interaction of several DNA binding domains, cofactors or modulators at transcriptional and post transcriptional level. So, it is very important to examine the detailed view of valuable transcriptional activities underlying the network of galactomannan formation.

Transcriptome profiling of developing seeds of guar (Naoumkina et al. 2007) and developing fenugreek endosperm (Wang et al. 2012) has improved our current understanding on the regulatory process involved in the biosynthesis of galactomannans. Wang et al. (2012) identified the set of genes (*PMI*, *PMM*, *GGT*, *ManS*, *UGE*, *GMP/ MGT*, *FK and SUS*) encoding the enzymes involved in galactomannan biosynthesis. They reported that most of the genes were expressed at high levels except *FK* and *SUS* (expression level of these two remain constant at days post anthesis) and a probable model was constructed to show the galactomannan metabolic pathway (Figure 2). This model also predicted that the developing seed utilizes sucrose to produce UDP-Glucose and fructose by the activity of Sucrose synthase (SUS) as described earlier. Joët et al. (2014) briefly investigated the biosynthesis process and regulation in coffee seeds (*Coffea arabica*) and concluded that the set of five co-expressed genes namely, *GGT*, *ManS*, *α-Gal*, *UGE* and *MGT* may function as a regulon in the core biosynthetic machinery for galactomannan.

In addition to this, the transcript levels of *SUS*, *GolS* and *SDH* were found to be positively correlated with those of core biosynthetic genes, suggesting their significant roles in maintaining the carbohydrates reservoirs during the process of galactomannan assembly. The raffinose family oligosaccharides (RFOs) are found to be stored in the vacuoles of the legume endosperm (Buckeridge and Dietrich 1996) and are majorly responsible for the transient accumulation of storage carbohydrates by which pool of UDP-galactose and GDP-mannose are replenished continuously for the formation of galactomannan (Joët et al. 2014). The first reaction of the RFO pathway is catalyzed by Galactinol synthase, encoded by *GolS* gene (Saravitz, Pharr, and Carter 1987) and *SDH* codes for an enzyme that catalyzes the formation of sorbitol using fructose resulting from sucrose cleavage (Doehlert 1987) (Figure 2). A recent study also revealed the importance of sucrose synthase (SUS) like protein through the analysis of protein interaction network involved in the metabolism of galactomannan (Hu et al. 2019). Expression levels of another set of genes like *GALK*, *β-Gal*, *GALM* and *GALT* were found to be high in endosperm, which indicates the involvement of these genes in regulating the metabolism of galactomannan (Hu et al. 2019).

Besides these primary developmental effects, the composition of endospermic galactomannan reserves can also be influenced by climate. It has been reported that lower temperature favors the formation of RFOs and sorbitol and delay the biosynthesis of endospermic galactomannans. These results suggested the tight interconnection between metabolism of galactomannans, RFOs and sorbitol at mid-developmental stages (Joët et al. 2014), but whether this trend is followed in other seeds enriched with galactomannan, remains to be determined.

The two transcription factor genes named as *NAC*10 and *NAC*75 were found to be up-regulated in the fenugreek endosperm (Wang et al. 2012). Transcription factors like NAC and MYB have shown to function as a master regulator for the activation of secondary cell wall biosynthesis (Zhong, Lee, and Ye 2010; Ambavaram et al. 2011). But in coffee seeds, none of them was shown to be expressed during accumulation of galactomannan. Instead, other transcription factor genes like B3 domain and AP2/ERF were up-regulated (Joët et al. 2014). The examination of novel genes through co-expression analysis in the cellulose biosynthesis pathway in *Arabidopsis* has been the most successful example so far (Persson et al. 2005). However, lack of large transcriptomic data sets in galactomannan-rich seeds have restricted the identification of novel transcription factors or binding domains governing the galactomannan metabolism.

Tyagi et al. (2018) reported that three novel miRNAs (*Ct*-miR3157, *Ct*-miR3130 and *Ct*-miR3135) served as important regulators in the process of galactomannan biosynthesis in guar seeds (Figure 2). They identified two novel genes

Table 4. Summary of composition of different leguminous seeds.

Crops	Seed coat (%)	Germ (%)	Endosperm (%)	Moisture content (%)	Protein content (%)	Ash content (%)	Fiber content (%)	Fat content (%)	Galactomannan content (%)	References
Carob bean	30-33	23-25	42-46	10-13	5	1	1	1	80-85	Maier et al. 1993; Mirhosseini and Amid 2012; Srivastava and Kapoor 2005
Guar	14-16	45	38-45	8-14	5-6	0.5-1	2-3	0.5-0.9	75-85	Maier et al. 1993; Mirhosseini and Amid 2012; Srivastava and Kapoor 2005; Sabahelkheir Murwan et al. 2012
Tara	38-40	27-30	30-34	15	3.5	1.5	2	–	73.9	Maier et al. 1993; Mirhosseini and Amid 2012; Borzelleca et al. 1993
Cassia	20-24	28-32	48-52	6-12	4-6	0.5-1.15	5-10	0.5-1	75-85	Chaubey and Kapoor 2001; www.cassiagums.com. . . . .

named as *ManS* and *UGE* and revealed that these two genes serve as potential targets for identified miRNAs.

Classification of galactomannans

The researchers principally studied these galactomannan gums owning to their biodegradable, sustainable and biosafe characteristics and categorized them on the basis of their origins, chemical structures and behaviors (Mirhosseini and Amid 2012). These plant-based gum exudates are well known for their chemical and functional properties and were introduced as potential industrial sources and also classified as a GRAS food ingredient.

Carob bean or locust bean gum

Among legumes, carob bean (*C. siliqua*) was the first widely used industrial crop for gelling purposes (Whistler 1993). *Ceratonia siliqua,* a tree indigenous to Spain, is also cultivated in larger quantities in Cyprus, Italy and other Mediterranean countries (Maier et al. 1993). In 2009, worldwide production of carob bean pods was estimated to be around 300,000–350,000 tonnes/year out of which 9,000–10,000 tonnes were consumed in the food industry (Wielinga 2009). Carob seed contains 30–33% husk, 23–25% germ and 42–46% endosperm (Mirhosseini and Amid 2012). Carob bean gum contains 10-13% moisture, 5% protein, 1% ash, 1% fat, 1% fiber, 80–85% galactomannan (Table 4). The molecular weight of carob bean gum ranges from 5×10^4 to 3×10^6 Da (Mahungu and Meyland 2008; Wielinga 2009). It possesses low galactose substitution (M/G ratio= 3.75) (Figure 3A) due to which it cannot disperse rapidly in water and thus have a higher tendency to interact with gelling polysaccharides like borax, agar, xanthan and carrageenan (Maier et al. 1993; Srivastava and Kapoor 2005). Maier et al. (1993) described the formation of gel by the use of carob bean which imparts an elastic character to gel and decelerate syneresis process.

Samil Kök (2007) studied and compared the compositional characteristics of low-quality crude carob bean gum (cCBG) and high-quality refined carob bean gum (rCBG) and reported that M/G ratio of cCBG and rCBG samples range from 3.1 to 3.9. The cCBG contain significant levels of arabinose, fat, protein and ash than those of rCBG, by which functional and gelling properties were affected and quality of gum was compromised. Due to the presence of non-galactomannan content, thermal stability of gum fraction of the crude and refined sample were also found to be different (Kök, Hill, and Mitchell 1999).

It was the first source of galactomannan with wide applications in food, paper, textile, pharmaceutical, cosmetic and other industries. This biopolymer has been commonly used as a stabilizer and thickener in dairy products (Dea and Morrison 1975) and also replaced the fat in many milk products due to its capability to form viscous suspensions at low concentration and maintain the stability of emulsions (Dakia et al. 2008).

Guar gum

Cluster bean (*C. tetragonoloba)*, also known as guar is an annually grown plant, cultivated in the arid and semi-arid regions of India and Pakistan as a food crop for animals and as a food ingredient for our consumption (Maier et al. 1993; Whistler and Hymowitz 1979). Guar seed consists of the husk (14–16%), endosperm (38–45%) and germ (45%) (Mirhosseini and Amid 2012). Guar gum contains 8–14% moisture, 5–6% protein, 0.5–1% ash, 0.5–0.9% fat, 2–3% fiber, 75–85% galactomannan (Table 4). The molecular weight of guar gum ranges from 5×10^4 to 8×10^6 Da (Mahungu and Meyland 2008) and is one of the naturally occurring polymer with the highest molecular mass and

water solubility (Maier et al. 1993). It possesses high galactosyl substituted side chain (M/G ratio= 1.54–2) (Figure 3B).

Guar gum contains several other non-galactomannan components which make it less water soluble and hence the derivatives obtained by modification of guar gum can compensate the disadvantages of natural gum (Wu 2009). Modifications include etherification, esterification and oxidation which complement the functional attributes of guar galactomannan (Wu 2009; Nishinari et al. 2007). For example, carboxymethyl modification may increase the hydrophilic nature and solution clarity of the gum solutions. Wu (2009) studied the flow behaviors of mixed solution of guar and carboxymethylated gum and reported that presence of carboxymethylated guar gum intensifies shear-thinning behavior and increases viscosity at a particular range of mixed ratios. This was due to change in the branched interactions among macromolecular chains in the structure of the galactomannans. Microcarriers and nanocarriers made of carboxymethylated guar gum using various formulations strategies like gelatin blending (Phadke, Manjeshwar, and Aminabhavi 2014) and cross-linking with trisodium trimetaphosphate (Dodi et al. 2016) are considered to be compatible drug delivery carrier.

When guar gum was modified to its hydroxypropyl form, the hydrogen-bonding sites present in the backbone structure gets blocked by the attached hydroxypropyl groups and reduces the formation of intermolecular hydrogen bonding in between the molecules (Cheng, Brown, and Prud'homme 2002). Aqueous solutions of its gum products form gels on treatment with crosslinking agents like borates and metal ions under controlled pH conditions. Unlike other gels, gels obtained from guar gum are slowly slump and flow when placed on flat surfaces (Maier et al. 1993). It is used to coat and stiffen paper because films formed by its gum have high tensile strengths than carob bean gum (Nishinari et al. 2007).

Guar gum is a vital crop for cosmetic industry because of its wide range of compatibilities and excellent properties (Mudgil, Barak, and Khatkar 2014). Traditionally, it is known to have beneficial roles in health related problems like heart disease, colon cancer, diabetes, bowel movements (Chudzikowski 1971) and in native formulations, but remains to be tested.

Fenugreek gum

This legume is native to Mediterranean regions and grown annually in the Middle East, Africa, and India. India accounts for 70–80% of total world production of fenugreek (Sakhare, Inamdar, and Prabhasankar 2015). Fenugreek is the richest source of soluble and insoluble fiber amongst all other gums (carob, guar, tara and cassia). Fenugreek seed consists of 6–7% fat, 23–26% protein and 58% sugars of which 25% is dietary fiber (US Department of Agriculture 2001) and in some cases, up to 48% (w/w) of dietary fiber have been reported (Brummer, Cui, and Wang 2003). As fenugreek contains a high proportion of protein, it is very important to extract the fenugreek gum in a purified form for its industrial use. The pronase enzyme treatment reduced the protein level to 0.6% from 2.36% in fenugreek gum (Brummer, Cui, and Wang 2003). The protein content was reduced to 0.16% from 3.74%, when treated with phenol solvent during the extraction procedure, much lower than all data reported so far (Youssef et al. 2009).

The M/G ratio ranged from 1.02 to 1.14 and molecular weight was found to be 1.41×10^6 Da by HPSEC (Brummer, Cui, and Wang 2003). The molecular weight and M/G ratio varied when different extraction procedures were used. The M/G ratio varied from 1.2 to 1.23, slightly higher than the value reported by Brummer, Cui, and Wang (2003) and molecular weight was 2.35×10^6 Da after an additional purification step with phenol solvent (Youssef et al. 2009).

Since the mannose residues in the backbone of fenugreek galactomannan are almost completely substituted with galactose side chains (Figure 3C) and hence are much more resistant toward enzymatic degradation in the digestive tract (Wielinga 2009). As fenugreek gum possess slow hydration rate, slow homogenous dispersibility and unpleasant flavor, extrusion cooking, an economical and efficient technology can be used in food processing to improve the hydration properties (water solubility, water hydration viscosity and water dispersibility) and to improve the soluble dietary fiber content of plant seed gums. Hence, the effect of extrusion process on fenugreek gum was studied by Chang et al. (2011). The hydration properties and unpleasant flavor of the gum was found to be improved significantly, but no considerable changes were seen in water holding and emulsion capacity because modification like extrusion has changed the conformational properties of gum due to which some hydrophilic groups got exposed to react with water. Other coworkers' experiments have supported these results by demonstrating the effect of extruded and non-extruded fenugreek gum on bread (Roberts et al. 2012).

Tara gum

This galactomannan is extracted from *Caesalpinia spinosa* (Tara), indigenous to northern regions of South America and Africa, primarily grown for commercial purposes exclusively in Ecuador, Peru (accounts for 80% of world production), and also in tropical East Africa. The complete compositional analysis of tara seeds revealed 38–40% husk, 30–34% endosperm and 27–30% germ, out of which 25% were lipids and 42% were protein (Table 4). Tara gum contains 15% moisture, 1.5% ash, 3.5% protein and 2% dietary fiber (Maier et al. 1993). The approximate molecular weight of tara gum is 1.0×10^6 Da (Santos et al. 2019). Borzelleca et al. (1993) assessed the basic properties of tara gum in order to use it as a food constituent and reported that the endosperm of tara seed was not completely removed from the germ and husk portion in the commercial productions. Instead, it may contain small amounts of fat and protein from attached germ portion and husk due to which large proportions of ash and insoluble acids were present in commercially produced tara gum. Tara gum has a M/G ratio of

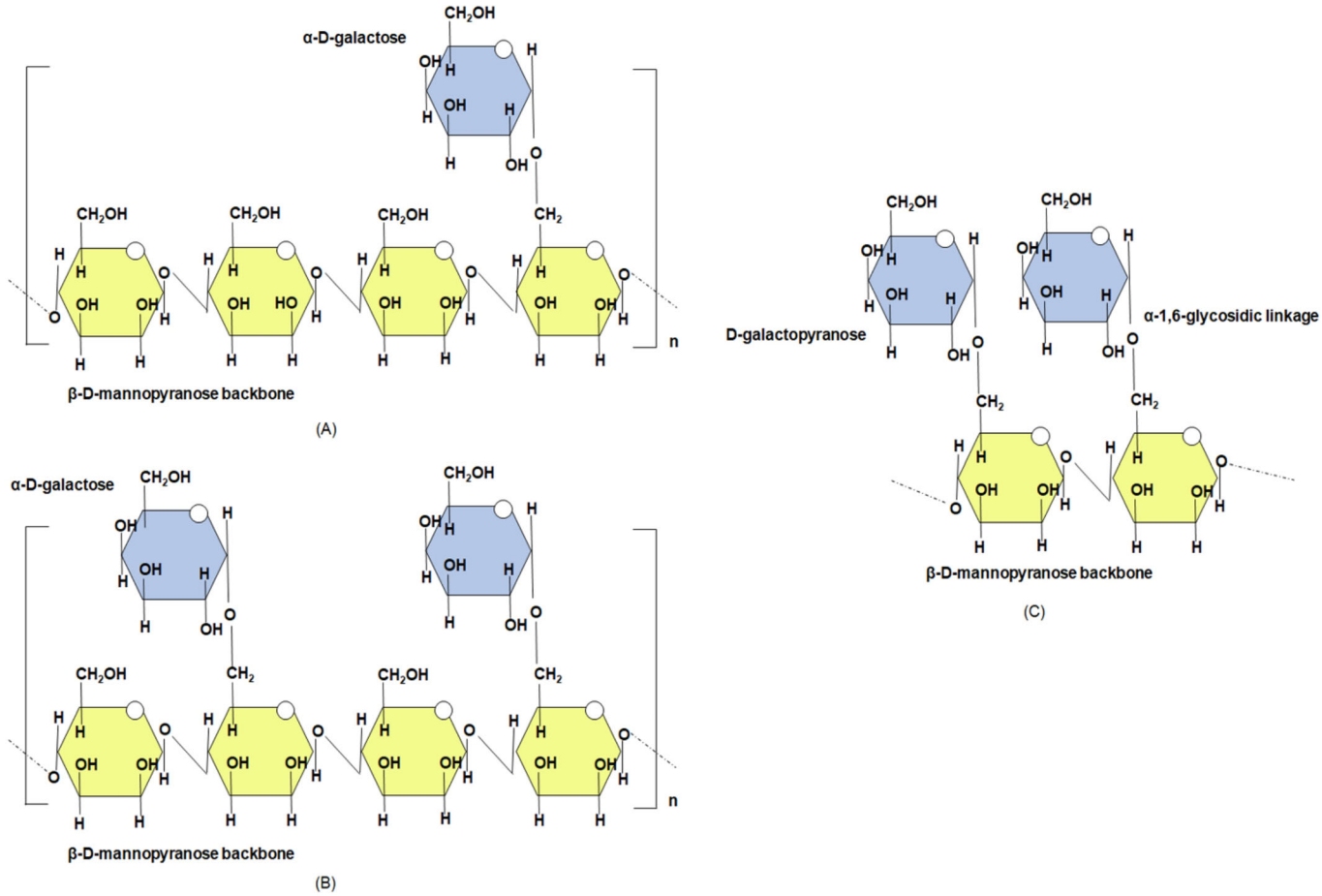

Figure 3. Structure of (A) Carob Bean Gum (B) Guar Gum (C) Fenugreek Gum.

3:1 (Figure 4A) and can attain high viscosity in water in a matter of minutes (Wu et al. 2015).

Recently, researchers have shown that the tara gum can be used in the manufacture of nanocomposite films when blended with cellulose nanocrystals and films prepared by this method possess high light transmittance, good mechanical properties, and least oxygen permeability (Ma, Hu, and Wang 2016).

Cassia gum

Cassia gum is mainly derived from the endosperm of *Cassia obtusifolia* and *Cassia tora*, which belongs to the Leguminosae family and native to subtropical regions of the world. Other species from which cassia galactomannan can also be isolated are *Cassia angustifolia*, *Cassia javahikai*, *Cassia pleurocarpa*, *Cassia javanica* (Mirhosseini and Amid 2012). Chaubey and Kapoor (2001) studied the compositional parameters of *C. angustifolia* and reported that the cassia seed consists of the seed coat (20–24%), endosperm (48–52%) and germ (28–32%). Gum isolated from this seed contains 10.6% protein, 4.1% ash, 5.8% ether extract, 34% water-soluble galactomannans etc. (Table 4). M/G ratio and molecular weight of galactomannans obtained from cassia seed varied from species to species. For example, in *C. tora* and *C. obtusifolia,* M/G ratio was found to be 5:1 (Figure 4B) and molecular weight varied from 2×10^5 to 3×10^5 Da (Mahungu and Meyland 2008) but in *C. angustifolia*, M/G ratio was found to be 2.9 and average molecular weight was 9.66×10^4 Da (Chaubey and Kapoor 2001).

The polymers formed from the cassia gum extracted from C. *javahikai* are biocompatible, biodegradable and are extensively used as a hydrocolloid (Singh, Srivastava, and Tiwari 2009b). The nonionic galactomannan isolated from *C. pleurocarpa* was found to have good water retention capacity, viscous enhancing properties and unique gelling ability which make them an excellent substrate for the tissue engineering, biomedical applications and drug delivery (Singh, Sethi, and Tiwari 2009a).

Galactomannan mobilization and control of M/G ratio

During seed development, the galactomannans get accumulated in the endosperm cell walls (Reid and Meier 1973b) and fills the void in fenugreek seed previously occupied by the protoplast and the deposition in cell-wall of endosperm continues until protoplast degenerates (Meier and Reid 1977). The non-living seed galactomannan in the endosperm is encircled by a layer of living cells called the aleurone layer when the deposition process is about to end (Reid 1971). At the time of seed germination, hydrolytic enzymes are produced by aleurone cells to metabolize the galactomannan (Reid and Meier 1972; Buckeridge and Dietrich 1996) but

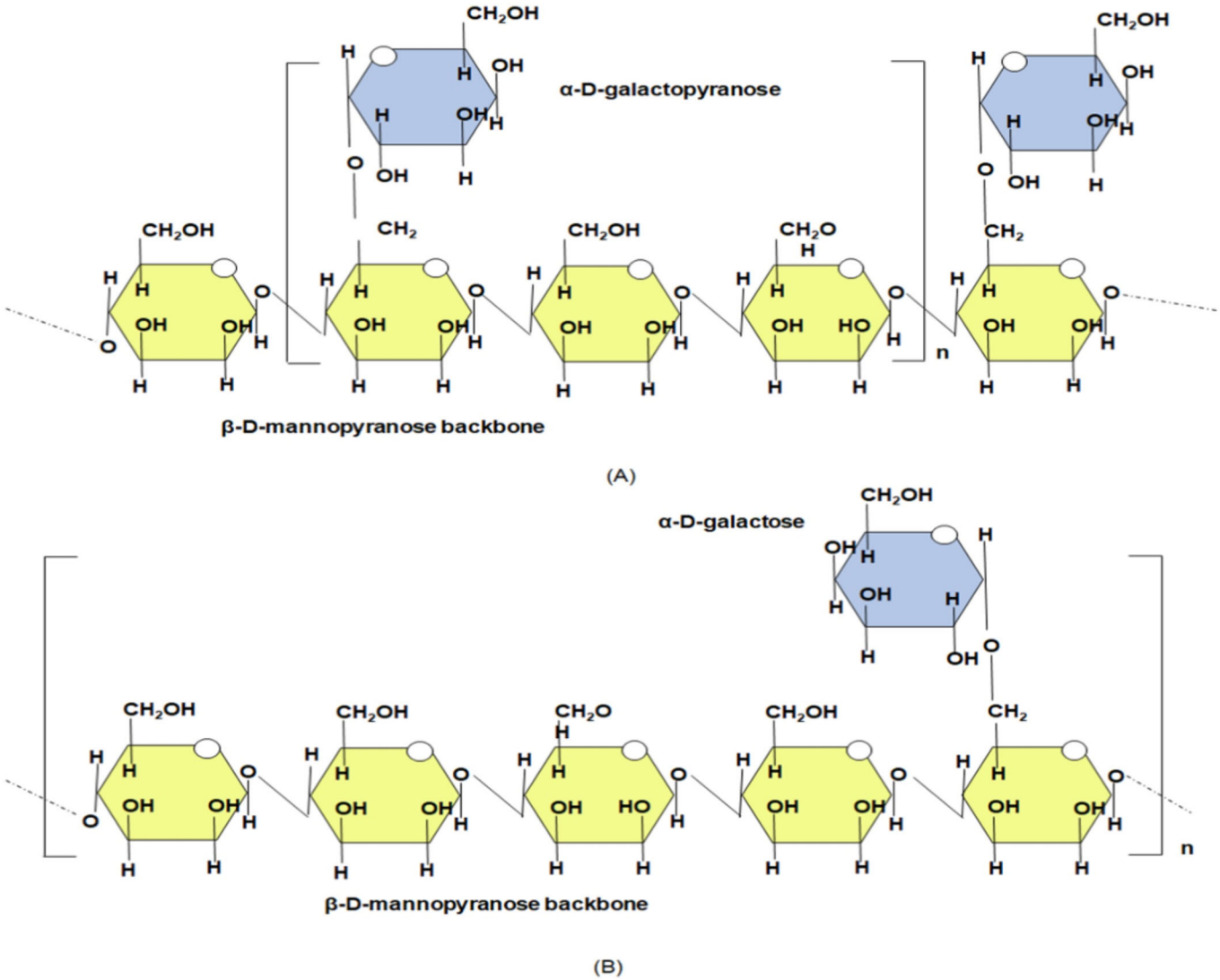

Figure 4. Structure of (A) Tara Gum (B) Cassia Gum.

not cotyledons (Buckeridge, Dietrich, and De Lima 2000). The main hydrolytic enzymes responsible for mobilizing galactomannan are: α-galactosidase which catalyzes the removal of (1-6)-α-D-galactose side chains, endo β-mannanase which promotes the random hydrolysis of (1-4)-β-D-mannan backbone chain into oligosaccharides and β-mannosidase which mediates the complete hydrolysis of the D-manno-oligosaccharides to D-mannose (Reid and Meier 1973a; Dea and Morrison 1975). There is no specialized aleurone layer in the carob seed but all the endosperm cells possess a living protoplast (Buckeridge, Dietrich, and De Lima 2000) while in case of guar seed, aleurone layer is made up of a thick layer of cells (McClendon, Nolan, and Wenzler 1976).

Leguminous seeds are found to be commonly enriched with α-galactosidases but are not confined to only those which contain rich amount of galactomannan (Reid and Meier 1973a). The formation of α-galactosidase is guided by aleurone cells during seed germination in guar plant (Hughes et al. 1988). McCleary and Matheson (1974) examined the changes in activity/specificity of α-galactosidases isolated from four germinating legume seeds (carob, lucerne, guar and soybean) to find out the substrate specificity and physiological function. They reported a rapid increase in the activity of α-galactosidase that corresponded to the time in which galactomannan was metabolized and then declined when all the galactomannan had been hydrolyzed. They checked the substrate specificity of different α-galactosidases with Lucerne galactomannan, melibiose, stachyose, raffinose and found that guar and lucerne α-galactosidases have high V_{max} values for lucerne galactomannan but this was not accounted for carob and soybean. High V_{max} values corresponded with their role in hydrolysis of galactomannan as carob and soybean contain low level of galactose as compared to lucerne and guar. During galactomannan biosynthesis, the levels of α-galactosidase purified from developing senna seeds (*Senna occidentalis*) increases dramatically upto late deposition phase and capable of removing galactose from galactomannan without prior depolymerization of the backbone but this was not observed for guar and fenugreek. It was suggested that senna α-galactosidase involved in the reduction of galactose content (or increase of M/G ratio) of the galactomannan and was one of the vital factor in addition to intrinsic properties and specificities of the other biosynthetic enzymes which controls the degree of galactose

Table 5. Galactomannan yields (percentage of the dry weight of the seed) of leguminous plants and their M/G ratio.

Species	Family	M/G ratio	Yield of gum (%)	References
Ceratonia siliqua (carob bean gum)	Caesalpiniaceae	3.75 3.8-5.7	38	Srivastava and Kapoor 2005; Dea and Morrison 1975; Buckeridge, Dietrich, and De Lima 2000
Cyamopsis tetragonoloba (guar gum)	Papilionaceae	1.54 1.7 1.4-1.8	35 23.5	Srivastava and Kapoor 2005; Dea and Morrison 1975; Buckeridge, Dietrich, and De Lima 2000
Caesalpinia spinosa (tara gum)	Caesalpiniaceae	2.7 3.0	24	Buckeridge, Dietrich, and De Lima 2000; Wu et al. 2015
Trigonella foenum graecum (fenugreek gum)	Papilionaceae	1.13 1.2-1.23 1.02-1.14	47	Srivastava and Kapoor 2005; Wielinga 2009; Youssef et al. 2009; Brummer, Cui, and Wang 2003
Cassia tora (cassia gum)	Caesalpiniaceae	3.0 5.0	–	Srivastava and Kapoor 2005; Buckeridge, Dietrich, and De Lima 2000; Mahungu and Meyland 2008
Cassia obtusifolia (cassia gum)	Caesalpiniaceae	5.0	–	Mahungu and Meyland 2008
Cassia angustifolia (cassia gum)	Caesalpiniaceae	2.9 1.5	34	Chaubey and Kapoor 2001; Buckeridge, Dietrich, and De Lima 2000
Cassia javanica (cassia gum)	Caesalpiniaceae	2.0	–	Buckeridge, Dietrich, and De Lima 2000
Sesbania bispinosa (dhaincha seed gum)	Papilionaceae	2.0	19	Srivastava and Kapoor 2005; Buckeridge, Dietrich, and De Lima 2000
Cassia pulcherrima	Caesalpiniaceae	2.7 3.0 1.9	24 31	Buckeridge, Dietrich, and De Lima 2000; Srivastava and Kapoor 2005
Gleditsia tricanthos (honey locust gum)	Caesalpiniaceae	3.2 2.71, 3.76, 3.82	15-20 27	Dea and Morrison 1975; Buckeridge, Dietrich, and De Lima 2000
Senna occidentalis (senna gum)	Caesalpiniaceae	2.3-3.2	–	Buckeridge, 2010

substitution of the final polysaccharides (Edwards et al. 1992). To understand this phenomenon, α-galactosidase gene from developing senna was expressed under the control of a wheat high molecular weight glutenin promoter in guar. Expressed senna α-galactosidase was able to hydrolyze the galactose residues in transgenic guar and demonstrated the relationship between α-galactosidase activity and reduction in the galactose content of galactomannan (Joersbo, Marcussen, and Brunstedt 2001). It was also observed that lack of α-galactosidase in the endosperm of macapuno cultivar of coconut leads to the formation of galactomannan with low M/G ratio as compared with the ratio present in non-mutants (Mujer, Ramirez, and Mendoza 1984).

Overbeeke et al. (1989) cloned and sequenced the α-galactosidase gene from guar plant and reported that it has a single polypeptide chain with a molecular mass of 40.5 KDa. On the basis of above results, α-galactosidases have found an important role in post depositional processes in determining the degree of galactosylation (M/G ratio) along the mannan backbone in legume seed like senna, which contains low degree of galactose substitution while in other species like guar and fenugreek (contains high degree of α-galactosyl side chain), ratio is determined at the biosynthesis step (Edwards et al. 1992). Investigation by Redgwell et al. (2003) supported the above results and indicated that the degree of substitution was found to be changed from flowering to mature stage in coffee beans also and hence M/G ratio is developmentally regulated by the action of α-galactosidase. The list of M/G ratio and galactomannan yield of different leguminous seed gums are given in Table 5.

In addition to α-galactosidases, β-mannosidases are also responsible for the galactomannan breakdown *in vivo* (Reid and Meier 1972; Reid and Meier 1973a). This was shown by assaying the activities of both enzymes from homogenates of dry isolated endosperms of fenugreek in combination with the absence or presence of metabolic inhibitors. Same type of experiments were done for investigating the role of endo-β-mannanases which concluded that regulation of activity of all three enzymes were controlled by the fenugreek aleurone layer and their activities increases in parallel with galactomannan depletion (Reid and Meier 1973a). A cDNA encoding an endo-β-mannanase was cloned from the seeds of germinated tomato seeds and it was observed that the encoded enzyme was not expressed in any part of the plant except endosperm (Bewley et al. 1997). McCleary and Matheson (1983) has purified the endo-β-mannanase from *C. tetragonoloba*. It was also reported that endo-β-mannanases are only confined to some leguminous seeds which contain galactomannan (Reid and Meier 1973) and vary significantly in their ability to hydrolyze galactomannans if isolated from different leguminous sources (McCleary and Matheson 1983).

The galactomannan mobilization confirmed that this polysaccharide is hydrolyzed into the simple monosaccharide units (free galactose and mannose) and used in the formation of sucrose, at the same time in the endosperm. This sucrose is then transported to the developing embryo for the fulfillment of carbon and energy requirements (Figure 5), while in cotyledons starch is transiently synthesized, and hence synthesis of starch and degradation of cell wall storage

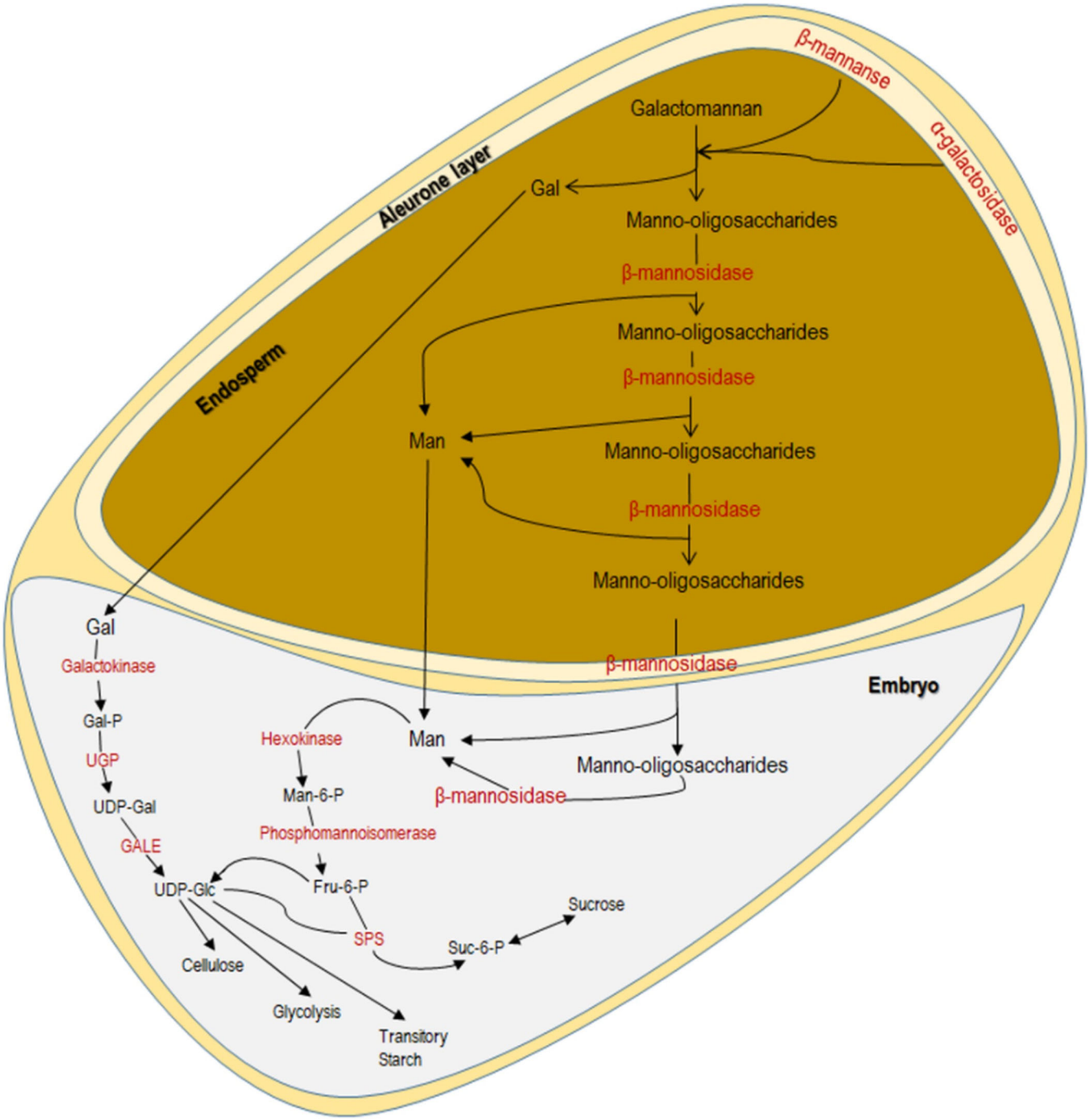

Figure 5. Biochemical routes involved in the galactomannan mobilization and utilization of released products by the developing embryo (adapted from Buckeridge, Dietrich, and De Lima 2000). Abbrevations: Man, mannose; Gal, galactose; Man-6-P, mannose-6-phosphate; Suc-6-P, sucrose-6-phosphate; UDP-Glc, uridine diphosphate glucose; UGP, UDP-galactose pyrophosphorylase; UDP-Gal, uridine diphosphate galactose; Fru-6-P, fructose-6-phosphate; SPS, sucrose phosphate synthase; GALE, UDP-galactose-4-epimerase.

polysaccharides might be interrelated (Buckeridge, Dietrich, and De Lima 2000).

McCleary and coworkers (McCleary et al. 1976; McCleary 1983) studied the fate of products produced from galactomannan degradation and suggested that the phosphomannoisomerase and phosphoglucoisomerase enzymes are responsible for the isomerization of mannose into glucose, and utilized for the formation of sucrose in the endosperm of guar seeds.

Extraction of galactomannan

Industrial method

Several authors have extensively reported about the extraction and purification procedure of galactomannan for industrial scale which can be used at laboratory scale with slight modifications (Dey 1978; Andrade et al. 1999; Bouzouita et al. 2007; Liyanage et al. 2015; Kontogiorgos 2017 and many more). Srivastava and Kapoor (2005) described the

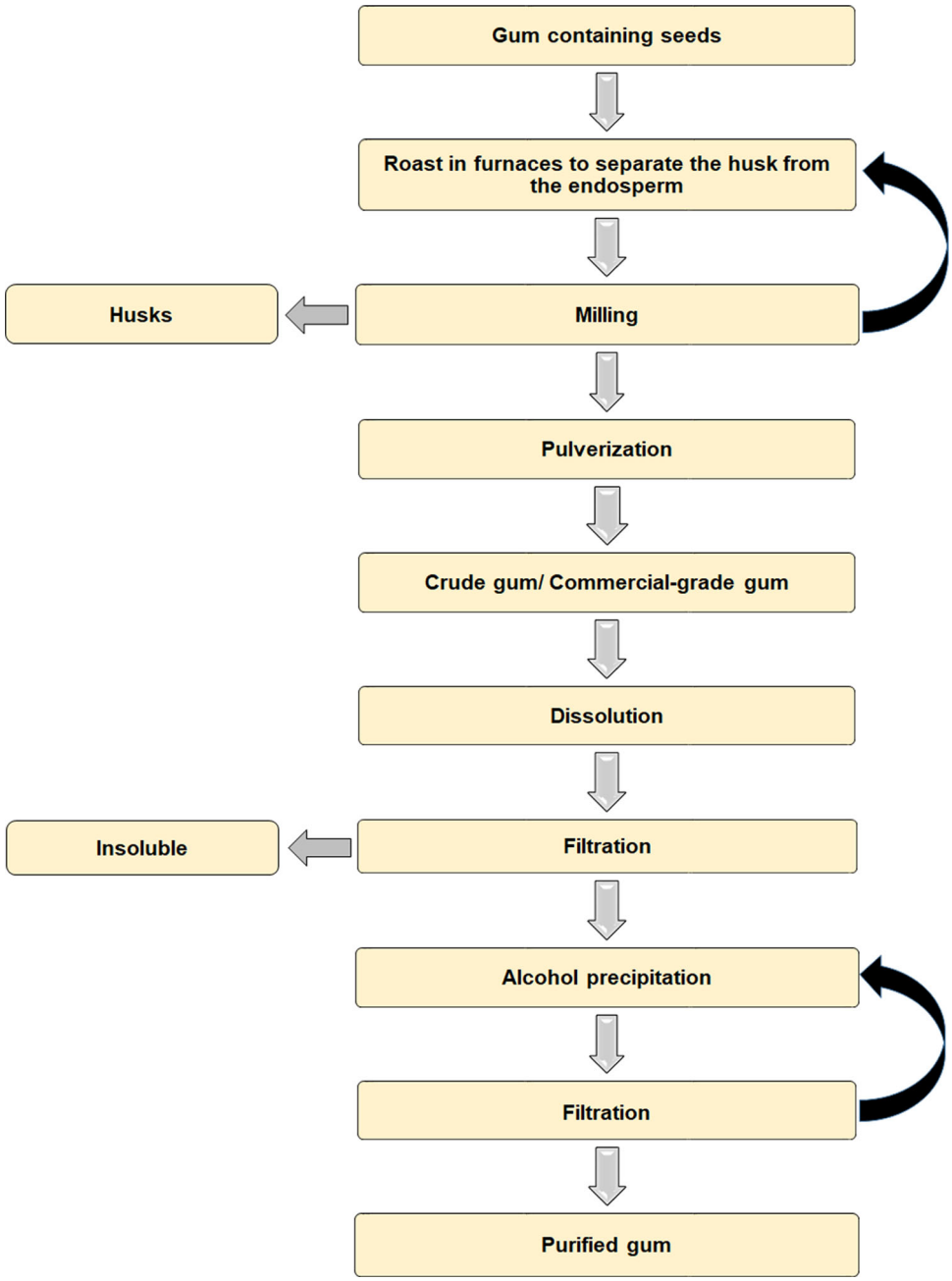

Figure 6. Flow chart representing the isolation and purification process of galactomannan.

general isolation and purification process used at commercial scale to extract the gum. Galactomannan containing seeds are roasted in furnaces to slacken the husk or seed coat from the endosperm and then the seeds are subjected to grinding in mills using specified mesh size sieves. The detached endosperm is then subjected to re-milling process as it is still attached with the hull and then pulverized to fine powdered form with desirable mesh size. Pulverization is a technique that can produce gum powder of less or more fine size depending upon the conditions applied (temperature, humidity and experimental set up etc.). The gum powder then obtained is the commercial-grade gum or crude gum. This crude gum is a mixture of impurities (protein, pectin, phytin, pentosan, ash and acid insoluble residue) and hence, subjected to purification process in order to improve its physicochemical properties. Several approaches can be used for the purification of crude gum powder but precipitation using ethanol is the most acceptable one while others using methyl alcohol, copper or barium complexes have also been reported (Bouzouita et al. 2007). Generally, gum powder is dissolved in water and can be precipitated fractionally using polar solvents and also can be purified with dialysis and membrane filtration (Srivastava and Kapoor 2005). The complete process of isolation and purification of galactomannan have been described in Figure 6.

Biochemical method

The extraction of galactomannan from flour or powder can be done with cold or hot water, alkali or dilute acid and purified using primary alcohols, copper complex, barium hydroxide, acetylpyridinium bromide, acetylation (Dey

1978), dialysis (Srivastava and Kapoor 2005; Hu et al. 2017) and deionized with column chromatography (Bhatia et al. 2013).

Quantification of galactomannan

Various methods have been reported for quantification of galactomannan content which include colorimetric and enzymatic methods.

Colorimetric method

Dubois et al. (1956) reported a sensitive method for the quantification of monosaccharides and their methylated components, oligosaccharides and polysaccharides, commonly called as Phenol sulfuric acid method. Phenol reacts with free reducing group of sugars in the presence of sulfuric acid and produces an orange-yellow color which can be measured spectrophotometrically at 490 nm.

Enzymatic method

This method is based on the quantitative hydrolysis of galactomannans to D-galactose and manno-oligosaccharides by using a combination of α-galactosidase and β-mannanase (McCleary et al. 1981). This technique involves the measurement of D-galactose content of galactomannan using galactose dehydrogenase. This method is rapid and accurate for quantification of galactomannan content as compared to colorimetric method.

Applications of galactomannan

Non-food applications

Paper industry- Galactomannans serve as fiber deflocculating and strengthening agents and their addition in small amounts to pulp can escalate paper production (Mudgil, Barak, and Khatkar 2014). Carboxymethylated gum, when used as wet-end additive exhibits magnificent hydrogen bonding effects and lightweight papers with excellent tightness can also be manufactured to avoid printing ink strike throughs (Prajapati et al. 2013).

Textile and oil drilling industry- Galactomannan is used as sizing agent in textile industry when combined with starch and utilized as an inimitable thickener in paints (Thombare et al. 2016). Hence, sharply printed patterns can be produced due to thickened dye solutions.

In oil drilling industry, galactomannans are used to rupture rocks by applying high pressure (hydraulic fracturing). The fracturing fluid become thickened on addition of gum solutions and carries sand into ruptured rock by which oil or gas easily flow into well bore (Mudgil, Barak, and Khatkar 2014).

Cosmetic industry- Galactomannans are used on a large scale in cosmetic industry due to their nontoxic properties. They are used in the manufacturing of hair shampoos, lotions, ointments and tooth paste to which they impart slip in extrusion and stabilize the system (Chudzikowski 1971).

Explosive industry- Galactomannan possess water blocking, gelling and swelling properties due to which it can be used as an additive in explosive industry. Nitroglycerin, ammonium nitrate, and oil explosives are mixed with gum solutions in order to maintain the explosive property even in wet conditions (Thombare et al. 2016).

Pharmaceutical industry- Natural gums are used in pharmaceutical industries for the production of beads, films, nano-particles, monolithic matrix systems, liquid and gel formulations, as well as in injectable and inhalable systems (Grenha and Dionísio 2012). Gums having high M/G ratio are widely used for the formulation of hydrogels-based oral delivery systems, multiparticulate and tablet systems. Galactomannan has anti-diabetic and hypolipidemic effect, reduces LDL (low density lipoprotein) cholesterol due to high soluble fiber content and hence act as a bioactive substance (Barak and Mudgil 2014).

Food applications

Bakery products- Galactomannans in combination with other novel nutritious ingredients and enzymes can be used in the production of bakery products (gluten-free) where they enhance crumb's loaf volume and its moisture content and may substitute the gluten for its viscoelastic properties (Anton and Artfield 2008). The addition of gum solution to suspension of wheat flour increases the trough viscosity, peak viscosity, final viscosity and setback values and lowers the pasting temperature. Wheat flour also witnesses an increase in dough development time and water absorption capacity on addition of gum solution (Barak and Mudgil 2014). In combination with starch, they are effective to suppress the shrinking, cracking and dehydration of frozen-pie fillings (Mudgil, Barak, and Khatkar 2014).

Beverages- For a broad pH range, many gum solutions show stability and are thus used as best thickener, stabilizer and also enhance the shelf life of beverages. Galactomannans possess surface active properties that can be exploited to use them as oil-in-water beverage emulsion stabilizers (Mikkonen et al. 2009).

Meat products- Galactomannans exhibit binding and lubricating capabilities and are used for the manufacturing of stuffed meat products and sausages by binding the pieces of meat together and suppress phase separation during heat treatments and enhance the yield through water management (Ercelebi and Ibanoglu 2010).

Dairy products- Galactomannans inhibit ice recrystallization and lactose crystallization when used in ice cream formulations during frozen storage of the products. They are used in the preparation of cheese spreads to avoid syneresis and to improve spreading and texture (Kontogiorgos 2017). For yoghurts preparation, they are used in reducing fat content by allowing the maximum interaction of themselves with protein and improve texture (Barak and Mudgil 2014).

Seasonings- Galactomannans are widely used in sauces, salad dressings, soups and in other liquid formulations as

Table 6. Outline of galactomannan applications in various industries and their functionality.

Industry	Functionality
Non-food applications	
Paper	Act as fiber deflocculant, dispersant, sizing and suspending agent, enhances paper strength because of strong hydrogen bonding
Textile	Thickener in paints and dye solutions, sizing agent (in combination with starch)
Oil well drilling	Hydraulic fracturing by controlling water loss, viscosity and mobility
Cosmetics	Act as compatible thickener and stabilizer in hair shampoos, lotions, ointments and tooth paste, helps in explusion of paste smoothly from the tubes and bottles
Explosive	Water proofing, gelling and additive agent
Pharmaceutical	Behave as stabilizers, matrix formers, solubilisers, binders, viscosity enhancers, drug release modifiers, disintegrators, bioadhesives, emulsifiers and suspending agents in formulations like nanoparticles, films, monolithic matrix, injectable, inhalable, hydrogels, tablets, multiparticulate, etc.
Food applications	
Bakery products	Gluten-free and wheat flour dough (enhances loaf volume, soften texture, moisture retention), frozen-pie fillings (suppress shrinkage, dehydration and cracking)
Beverages	Soft drinks (thickener, stabilizer), oil-in-water emulsions (emulsifiers)
Meat products	Sausages, frozen and stuffed meats (binder, lubricant, consistency improvement and control syneresis)
Dairy	Ice-creams and milk desserts (inhibit ice recrystallization and lactose crystallization), Cheese spreads (control of phase separation and texture modification) low fat yoghurts (thickener, stabilizer and improve texture)
Seasonings	Salad dressings, sauces, mayonnaise and soups (improve consistency, control syneresis and fat reduction)
Films	Biodegradable films, fresh-cut fruits (improve shelf life by coatings)

well where they control the consistency, mouth feel, and stability of the dispersions. They increase the shelf-life of sauces by controlling phase separation of the solids and syneresis process (Kontogiorgos 2017).

Edible films- Galactomannans with lower galactose content are used to form edible films and exhibit biodegradability and thus provide a way to prevent minimal processing on fresh vegetables, fruits and meat products (Vargas et al. 2008). Properties of biopolymers like oxygen permeability, carbon dioxide permeability, moisture permeability needs to be tuned in order to produce films with high tensile strength and higher elongation at break and hence, galactomannans provide this fine tuning by varying the molecular structure of biopolymer (Kontogiorgos 2017). A descriptive outline of applications of galactomannan in various industries has been described in Table 6.

Conclusions

Galactomannans are the reserves of storage sugars, found in the endosperms of leguminous and non-leguminous seeds and utilized for the growth of an embryo during seed germination. They disperse easily in water and provide highly viscous and stable aqueous solutions. The M/G ratio determines the water solubility of galactomannans and can be altered in order to manipulate the physicochemical properties in agronomically and commercially important crops and gums of best quality can be obtained for the betterment of consumer goods. Significant clues have been obtained in identification of genes involved in the biosynthesis of hemicellulosic polysaccharides. However, the mechanisms by which the formation of mannan backbone is initiated and interactions between the polymer chain and other proteins to promote folding and stability of the functional complex remains unknown. Therefore, immense attention is required toward this important pathway by which genes with cohort relationship governing galactomannan biosynthesis and transcriptional regulatory network can be discovered and fully characterized. Amongst all major sources, guar bean tops as the best source of edible gum both in terms of quality and quantity. Moreover, extraction methods and complete functional characterization of guar gum provides valuable clues to its effective utilization across a range of industries.

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Disclosure statement

The authors declare no conflicts of interest.

Author contributions

K. Gaikwad conceived and designed the structure of the manuscript. P. Sharma complied and analyzed the literature and drafted the manuscript. S. Sharma reviewed and contributed to the text. G. Ramakrishna and H. Srivastava contributed in the preparation of the tables and figures. K. Gaikwad reviewed and finalized the manuscript. All authors read and approved the final manuscript.

Author note

Kishor Gaikwad, ORCID ID: https://orcid.org/0000-0002-0484-3844

ORCID

Kishor Gaikwad http://orcid.org/0000-0002-0484-3844

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