



A Glimpse of Galactomannans

Carbohydrate molecules have complex structures. These are the most abundant of the natural products and the source of all biological energy. Being poly functional in nature, these molecules participate in a multitude of chemical and biochemical reactions. They are composed of the polyhydroxy aldehydes, ketones, alcohols, acids and their simple derivatives as well as their polymers having linkages of the acetal type.

Carbohydrates can be classified in to *monosaccharides*, *oligosaccharides* and *polysaccharides*. Monosaccharides are the lower members of carbohydrates, which cannot be degraded by hydrolysis. Oligosaccharides and polysaccharides are polymers of monosaccharides and their derivatives, joined by acetal-type linkages. Oligosaccharides contain between 2 to 10 monosaccharide units, and polysaccharides contain more than 10 units.

Since antiquity, polysaccharides have been extracted or isolated from plant seed sources such as locust bean, guar, tara and tamarind. These polysaccharides or gums are derived from the endosperm of various plants (mainly from *Leguminosae*) seeds, where they function as reserve materials utilized during germination. Most of these polysaccharides share basic structural similarities, known as galactomannans.

Occurrence

The majority of galactomannans originate from *Leguminosae* family. 70 species of the *Leguminosae* have been identified containing galactomannans (Table 1). True galactomannans, as defined by *Aspinall*⁹ (that is, those mannans containing more than 5% of D-galactose) have also been extracted from members of *Annonaceae*, the *Convolvulaceae* and the *Palmae*, *Ebenaceae* and *Loganiaceae* as shown in Table 2.

Table 1. Galactomannans of *Leguminosae* species

Botanical name		M/G ratio
Subfamily	Species	
CAESALPINIACEAE	<i>Cassia absus</i>	3.00
	<i>C. emarginata</i>	2.70
	<i>C. Fistula</i>	3.00
	<i>C. leptocarpa</i>	3.05
	<i>C. marylandica</i>	3.76
	<i>C. nodosa</i>	2.7-3.5
	<i>C. occidentalis</i>	3.00
	<i>C. tora</i>	3.00
	<i>Ceratonia siliqua</i>	3.75
	<i>Caesalpinia cacalaco</i>	2.50
	<i>C. pulcherima</i>	2.7
	<i>C. spinosa</i>	-
	<i>Cercidium torreyanum</i>	3.38
	<i>Delonix regia</i>	4.28
	<i>Gleditsia amorphoides</i>	2.5
	<i>G. triacanthos</i>	3.2
	<i>Gymnocladus dioica</i>	2.71
	<i>Parkinsonia aculeata</i>	2.70
MIMOSACEAE	<i>Besmanthus illinoensis</i>	2.69
	<i>Leucaena galauca</i>	1.33
FABACEAE	<i>Sophora japonica</i>	5.19
	<i>Genista raetam</i>	4.14
	<i>G. scoparia</i>	1.59
	<i>G. cretica</i>	1.56-167

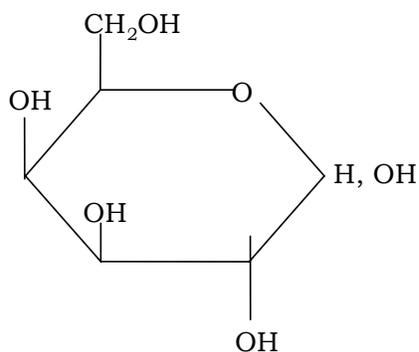
	<i>G. foenum-graecum</i>	1.2
	<i>G. hamosa</i>	1.17
	<i>G. monspeliaca</i>	1.08
	<i>G. polyserata</i>	1.13
	<i>G. radiata</i>	1.17
	<i>Anthyllis vulneraria</i>	1.33
	<i>Lotus corniculatus</i>	1.25
	<i>L. pedunculatus</i>	1.04
	<i>L. scoparius</i>	1.13
	<i>Alysicarpus veginalis</i>	1.14
	<i>Desmodium pulchellum</i>	2.00

Table 2. Galactomannans of non-leguminous plants

Botanical name		M/G ratio
ANNONACEAE	<i>Annona muricata</i>	4.46
CONVOLVULACEAE	<i>Convolvulus tricolor</i>	1.75
	<i>Ipomoea muricata</i>	1.8
EBENACEAE	<i>Diospyros virginiana</i>	-
LOGANIACEAE	<i>Strychnos nux-vomica</i>	-
PALMAE	<i>Borassus flabellifer</i>	2.4
	<i>Cocos mucifera</i>	2.57
	<i>Arenga saccharifera</i>	2.26
	<i>Phytelephas macrocarpa</i>	50
	<i>Hyphaene thebaica</i>	19
	<i>Phoenix dactylifera</i>	10

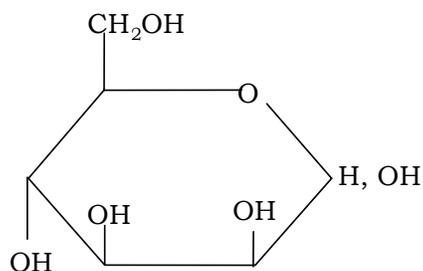
Physical properties of galactomannans

For a better understanding of properties of galactomannans one should know the basic structure of their building units.



Galactose

[4]



Mannose

It is obvious that mannose is provided with cis-OH groups in the galactomannan polymer. Therefore, an enhanced deposition to form hydrogen bonds between the polymannan chains is expected as long as neighbouring groups like galactose do not develop steric hindrance to prevent the galactomannan chains from coming too closer together and prevent the mannose cis-OH groups in forming the hydrogen bonds.

Comparing the different galactomannans of Table 3, it is obvious that, since additional cross linking via hydrogen bonds goes hand in hand with less solubility, an increase in substitution leads to higher solubility.

The best solubility is found with galactomannan-1, 1 in which the high substitution by galactose obviously establishes so much steric hindrance that it dissolves easily in cold water and prevents attack for some time for degrading enzymes.

Table 3. Chemical structure of polymannan and galactomannans

Polymannan	-M-M-M-M-M-M-M-
Galactomannan-1, 5 (<i>Cassia</i> gum) from the endosperm of <i>Cassia tora/obtusifolia</i>	-M-M-M-M-M-M-M-M-M-M-M- G G G
Galactomannan-1, 4 (Carubin) from the endosperm of <i>Ceratonia siliqua</i>	-M-M-M-M-M-M-M-M-M-M-M- G G G
Galactomannan-1, 3 (Tara gum) from the endosperm of <i>Cesalpinia spinosa</i>	-M-M-M-M-M-M-M-M-M-M-M- G G G G
Galactomannan-1, 2 (Guaran) from the endosperm of <i>Cyamopsis tetragonoloba</i>	-M-M-M-M-M-M-M-M-M-M-M- G G G G G G G G G
Galactomannan-1, 1	-M-M-M-M-M-M-M-M-M-M-M- G G G G G G G G G G G
M = Mannose, G = Galactose	

However, galactomannan-1, 2 where on average each second mannose unit is blocked by galactose, shows so much steric hindrance and so little hydrogen bonding between the molecular chains that it hydrates instantly.

Polymannan for example is almost insoluble in cold as well as in hot water and galactomannan-1, 5 shows only partial solubility in cold water resulting in a low viscosity. After boiling, the same suspension yields a thick, colloidal solution of high viscosity. This is caused by the thermal breakdown of the inter-molecular hydrogen bonds so that water can penetrate in between the chains leading to hydration of the molecules.

Galactomannan-1, 4 does not dissolve in cold water but its solubility in boiling water is already better than that of galactomannan-1, 5 due to slightly higher degree of substitution by galactose side groups compared to galactomannan-1, 5.

From the foregone discussion, it can be concluded that galactomannans-

- are rich in hydroxyl groups; this enables them to bind and take up water.
- rich in cis-OH groups, which allow aggregation from chain to chain via hydrogen bonding so that hydration becomes more complicated if interchange cross linking can take place.

By substitution with galactose, nature establishes steric hindrance between the molecules and thus enhances water solubility.

Technical applications of galactomannans

The world figures of galactomannan consumption differ quite considerably according to different sources. According to one estimate, around 90-100 thousand tons are consumed per year. The biggest consumption being that of guar gum with 70-80 thousand tons followed by locust bean gum with 12-14 thousand tons.

Reviewing the technical applications, attention is drawn to the chemical behavior of the different galactomannans. There are applications, which benefit from the excellent viscosity formation of some galactomannans or their derivatives and there are also applications, which benefit from water absorption or from the formation of hydrogen bonds as well as gel formation.

Viscosity development

Some galactomannans, especially guar, but also *Cassia* and locust bean gum and their derivatives (anionic, cationic and nonionic) develop very high viscosity in aqueous solution. In the textile industry they are used to thicken the dyebaths in printing and dyeing of fibers, fabrics and carpets. The gums control the flow characteristics of the dye formulations, so that sharp, bright patterns can be achieved. For different types of cloth and dyestuff, different types of thickener are used- mostly in combinations.

In the field of explosives, guar gum and derivatives are used to thicken nitrate salt solutions, which are the basic components of slurry explosive formulations. These compositions are safer to use and can be formulated to demand as a viscous liquid or even as gels.

It is well known that cracking and opening up the oil or gas bearing zones with hydraulic pressure can increase the productivity of oil and gas. Hydroxypropyl guar solution and other derivatives are used in this process which is known as hydraulic fracturing.

In this aspect another property of galactomannans is also of advantage: the ability to gel with elements like boron or transition metals in the form of their salts, which can be used to block or tighten wells. Since this gelling reaction is reversible with change of pH, it is used to control fluid loss in well.

Gel formation

Galactomannans are able to form gels with certain metal salts. This effect is used in the field of textiles to print vat-dyestuffs in two phases, which yields bright and sharp prints.

On the other hand galactomannans affect carrageenan and agar gels which diminish from one galactomannan to another in the direction of increasing galactose content. Thus it can be assumed that the mannose residue of the main chain is mainly involved. Therefore, only galactomannans with little or no steric hindrance by galactose groups may show this effect. Such properties will be useful not only in food and pet food but also in technical applications, where gels are used to bear and bind odors, as in solid air fresheners. Transport of solid powders like coal or ores suspended in such gels through pipeline could also be possible as these gels have excellent suspending force, which can be destroyed immediately when reaching the final point of destination by heating to only about 50°C.

Hydrogen bond formation

Easy hydrogen bond formation is one of the characteristics of galactomannans. This is used widely in the paper industry where guar has replaced locust bean as wet end additive.

Galactomannans replace the natural hemicellulose in paper bonding. Since galactomannans absorb onto the hydrated cellulose fibers, as the hydrogen bonding effect is one of the major factors in fiber bonding. Machine speed is increased by using galactomannans and the retention of fine fibers during the process is also increased.

Carboxymethyl derivatives of *Cassia* gum also show excellent hydrogen bonding effects, especially when used as wet-end additives and as sizing agent in paper manufacturing. Thus lightweight papers can be produced with excellent tightness, so that printing inks can not strike through.

In the mining industry galactomannans are used as chemical flotation agents by getting absorbed onto hydrated mineral surfaces. In flotation, the galactomannan functions as depressant to block the absorption of other reagents onto the surfaces of talc and other gangues, which are mined along with the valuable minerals.

Water absorption

To protect water sensitive goods, they may be spread with galactomannan powder and then packed. Dry guar is used to cover substances to prevent water from entering into cartridges filled with explosive powders, cables and so on.

Cross linked galactomannan derivatives can be used in competition with synthetic polymers as absorbents for hygiene articles.

Obviously, the applications of galactomannans depend more or less on their ability to form hydrogen bonds, a property which is counter played by steric effect of galactose side groups, which help to achieve increased solubility.

During the last several years many plant species have been investigated for their galactomannan contents to improve their properties by chemical modification and increase their utilization.

Table 4. Industrial uses of galactomannans

Industry	Product	Gum	Function
Food	-	Carboxymethylated guar gum	Thickening and gelling agents
	-	Carboxymethylated locust bean gum	Soluble and insoluble fibers
	Desserts	Xanthan-Tara gum mixtures	Synergistic effects
	Jelled puddings	Xanthan-Locust bean gum mixtures	Synergistic effects
	Ice cream	Guar gum with carrageenan and carboxymethyl cellulose	Stable thixotropic-stabilizer-emulsifier system
	Acidified dairy products	Guar and locust bean gum	
	Ice cream	Locust bean gum with alginate and gelatin	Allows high temperature treatment
Pharmaceutical	Vitamin B ₁₂ preparation	Guar gum	Stable water soluble preparation
	Preparation for treatment of gastrointestinal ulcers and diarrhea	Guar gum	Synergistic activity with bismuth salt
	Sustained release drugs	Guar gum	Guar gum (M.W. 280,000) releases ascorbic acid after 2.75 h; M.W. 50,000, after 2.0 h
	Tablet preparation	Guar gum	Dry binder
	Micro-encapsulation of drugs	Guar gum	High resorptivity of drug
Cosmetics	Hair decipher, hand towels, tissues	<i>Gleditsia triacanthos</i> gum	Treated with acroliein to give paper strengthener
Paint	Paint	Hydroxypropyl/hydroxyethyl ethers of galactomannans	Viscosity stabilization of poly(vinyl acetate) latex paints
Oil well drilling	Oil bores	Guar gum cross linked with borax, Hydroxypropyl guar gum	Stable, super elastic liquid with lessened temperature sensitivity, for control of lost circulation in oil field drilling operation for plugging leaks
	Oil, gas water bores	Guar-xanthan gum mixture	Stabilization of crosslinkage
Explosives	Explosive gel	Guar gum	Improved resistance to water and aging

Fire fighting	Air drop, forest fire control	Guar gum with decyl sulfate and ammonium phosphate solution	Provides viscosity stability
Building	Plaster	Guar and locust bean gum	Thickening agent
Paper Textile	Sizing	Calcium salts of carboxymethylated galactomannans Guar and locust bean gum	DS 0.6-1.6. Viscosity doubled and thixotropic surface increased from 0-16,766 dynes.cm ⁻² sec ⁻¹ Cross linked with transition metal ions; viscosity increases one hundred folds

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