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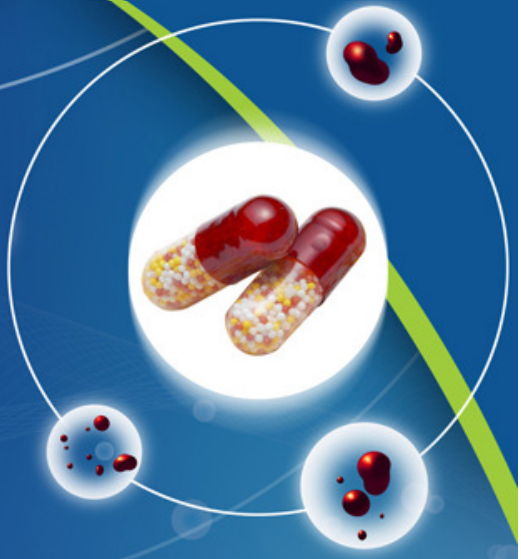

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Review Article

TAMARIND SEED POLYSACCHARIDE AND ITS RECENT APPLICATIONS: A REVIEW

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ABSTRACT

Controlled release drug delivery systems are preferred over from conventional oral drug delivery in the last few decades becauseof their clinical benefits over the later one. Hydrophilic matrix drug delivery systems prepared using natural polysaccharides are better alternative for developing sustained release formulation. One of such polysaccharides is Tamarind seed polysaccharide (TSP) isolated from seed kernel of Tamarindus indica. Although TSP is used as an ingredient in food materials, it has not been extensively evaluated till date for its utility in pharmaceuticals formulations. So, this review mainly focuses on the utility of TSP as an excipient in novel drug delivery systems.

KEYWORDS: *Crosslinking, Tamarind Seed Gum, Tamarind Seed Polysaccharide, Xyloglucan.*

INTRODUCTION

In recent years a lot of attention has been paid to the polymers which are derived from plant origin because of its wide and diverse applications in the pharmaceutical industries as binder, diluent, disintegrants in tablets, thickening agents in oral liquid solutions, as a protective colloids in suspensions, gelling agents in gels, and bases in suppositories [1]. They also have few other important applications like in the field of paints, textiles, cosmetics and paper industries [2]. Polysaccharides derived from plant origin are advantageous over synthetic polymers because they are biodegradable, biocompatible, nontoxic, low cost, ecofriendly processing and acceptable by the regulating authorities.

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Many polysaccharides are used because of their promising uses in drug delivery applications, some of which include acacia, chitosan, Ispagol, xanthan gum, guar gum, and many more [3]. An important natural polysaccharide amongst these is Tamarind seed xyloglucan which is also known as Tamarind seed polysaccharide (TSP) which is obtained from the seed kernel of Tamarindus indica. It possesses properties like high viscosity, broad pH tolerance, non-carcinogenicity, mucoadhesive nature and biocompatibility. It is used as stabilizer, thickener, gelling agent and binder in food and pharmaceutical industries.

TAMARIND SEED POLYSACCHARIDE

The seed kernel of the plant Tamarindus indica contains a xyloglucan/gum called tamarind seed gum. The polysaccharide which is present in tamarind seed gum is known as tamarind seed polysaccharide (TSP). Gum is present in the tamarind seed and it is a hydrophilic polymer which had been used as gelling,

thickening, suspending and emulsifying agents [4-7]. TSP constitutes about 65% of the seed components [8-10]. It is also used as a thickening, stabilizing and gelling agents in food [11]. The gum is also used as a binder in pharmaceutical tablets, as a humectants and emulsifier in the different types of formulations [12].

In recent times, tremendous amount of research is carried out in field of plant derived biocompatible polymeric material in designing of a dosage form for oral controlled release administration. The TSP is one such polymer which the pharmaceutical industries use and it is act as a binder in tablet dosage form, ocular drug delivery system and in sustained release drug delivery systems. Because of its novel mucoadhesive property, it can be also used in the delivery system for the ocular administration of hydrophilic and hydrophobic antibiotics.

METHODS OF ISOLATION AND EXTRACTION OF TSP

Method 1 [13]

200 g of tamarind seeds must be soaked in double distilled water and boiled for 5 h to remove the outer dark layer. After the outer dark layer is removed, sufficient amount of double distilled water should be added to the inner white portion and boiled with constant stirring in order to obtain the slurry. Now the resultant solution is cooled in refrigerator so that most of the undissolved portion settles down. The supernatant liquid can be separated out by simple decantation or centrifugation at 500 rpm for 20 min. Later the solution is concentrated on a water bath at 60°C to reduce the volume to one-third of its initial volume. The solution is now cooled and poured into 3 volumes of acetone by continuous stirring. Precipitates obtained must be washed with acetone and dried in vacuum at 50-60°C.

Method 2 [14]

Tamarind seeds must be collected and dried in sunlight. The kernels should be crushed into fine powder. 20 g of fine kernel powder is to be added to 200 ml of cold distilled water to prepare slurry. The slurry obtained must be poured into 800 ml of boiling distilled water and boiled for 20 min on a water bath to obtain a clear solution which must be kept aside overnight. The thin clear solution was then centrifuged at 5000 rpm for 20 min to separate all the foreign matter. Supernatant liquid was separated and poured into excess of absolute alcohol with continuous stirring. Precipitates obtained were collected by a suitable method and washed with 200 ml of absolute ethanol and dried at 50°C for 10 h. Store the polymer obtained in a desiccator.

Method 3 [15]

It involves the separation of tamarind kernel powder on the basis of their size distribution. Tamarind kernel powder (TKP) was defatted by using C-6 or C-8 aromatic hydrocarbons or C-1 or C-2 or above halogenated lower hydrocarbons or C-1 or C-5 mono or dihydroxy alcohols, e.g. ethylene dichloride, heptanes, or toluene. For defatting, Crude TKP is suspended in a suitable solvent to extract fat that is mechanically recovered by filtration or centrifugation and dried. After drying, HiSil or other siliceous materials like CabOSil are used to improve the flow properties of powder. The powder is further grounded by using Hammer mill or Pin mill that will reduce the size of the powder below 100 mm. The powder is further air classified by using suitable air classifier.

Method 4 [34]

Total of 5 g Dry Tamarind Kernel Powder (TKP) (dry basis) was mixed with 5 mL 95% (w/v) ethanol in a 500 mL beaker first and then 245 mL deionized water were added. Ethanol addition improves dispersion and prevents the agglomeration of TKP. The temperature being maintained at 37^{o}C using a circulating water bath with constant stirring using a magnetic stirrer. Protease at 0.16, 0.48, and 0.80 units/mL(U/mL) was added to the slurry and the reaction took place for 1, 3, and 5 h. After the protease digestion step, the suspension was separated using centrifuge (1500 x g, 10 min) and the supernatant was removed carefully. Then, the precipitate was mixed with 50mL of 95% (w/v) ethanol and stirred for 5min. The precipitate was separated from solvent by Whatman filter paper nr 1

under vacuum. After that, the isolated TSP (ITSP) was dried at room temperature, passed through a 150-*f*Êm stainless steel sieveand stored in a desiccator at room temperature for further analysis.

CHEMICAL COMPOSITION AND CHEMICAL STRUCTURE

The composition of tamarind kernel powder includes 12.7-15.4% of protein, 3-7.5% of oil, 7-8.4% of crude fiber, 61-72.2% carbohydrates, and 2.45-3.3% of ash. All of this was measured on dry weight basis. Chemically, tamarind kernel powder is a highly branched carbohydrate polymer. TSP is a polymer with an average molecular weight of 52350 Daltons and a monomer of mainly three sugars- glucose, galactose and xylose in a molar ratio of 3:2:1. The polymer consists of cellulose-type spine which carries xylose and galactoxylose substituents. About 80% of glucose residues are substituted by xylose residues (1-6 linked), which themselves are partially substituted by p-1-2 galactose residues. The exact sequential distribution of branches is not known. TSP is a branched polysaccharide with a main chain of Â-D-1-glucopyrynosyl units, with a side chain consisting of single D-xylopyranosyl unit attached to every 2nd, 3rd and 4th D glucopyrynosyl unit through1-6 linkage as depicted in Figure 1 [16].

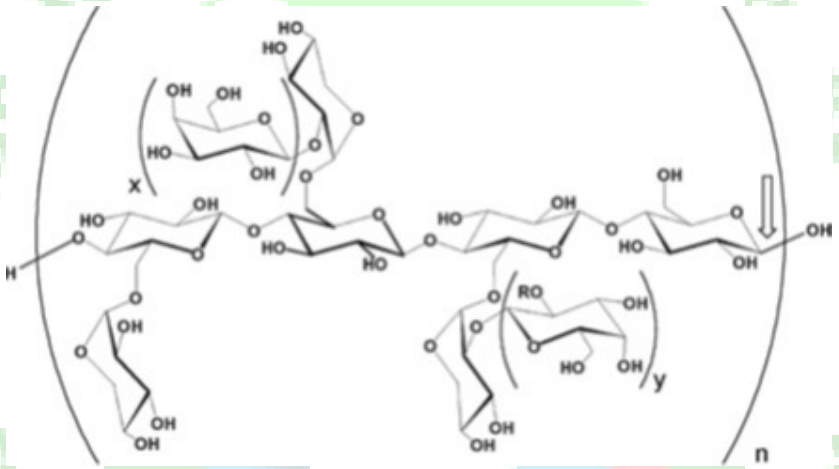

Figure 1: Chemical Structure of TSP

GENERAL PROPERTIES OF TAMARIND SEED POLYSACCHARIDE

TSP in its pure form is a high-molecular-weight, neutral branched polysaccharide consisting of cellulose like backbone that carries xylose and galctoxylose substances [17]. Its chemical residues are similar to that of mucin MUC-1 and Epsialin [18]. It is insoluble in organic solvents and dispersible in warm mater to form a highly viscous gel as a mucilaginous solution with a broad pH tolerance and adhesivity [17]. In addition, it is non-toxic and non-irritant with a haemostatic activity. It is a galactoxyloglucan, belongs to the xyloglucan family, and possesses properties such as non-Newtonian rheological behavior, mucomimetic, mucoadhesive and pseudo plastic properties [16].

CHEMICAL MODIFICATIONS OF TAMARIND SEED POLYSACCHARIDE (TSP)

Carboxymethylation of TSP

Carboxymethyl TSP is a modified derivative of TSP and the microbial resistance of CM-xyloglucan is far greater than TSP. The viscosity of CM- xyloglucan in solutions is also higher compared to native gum. Modification of the xyloglucan disrupts the organization and exposes the polysaccharide network for hydration thus increasing hydophilicity which results in higher viscosity due to this it's swelling index is also higher as compared to Xyloglucan. The presence of carboxymethyl groups makes the molecule resistant toward enzymatic attack [19]. Since

carboxymethyl xyloglucan possessenhanced properties necessary for the retardation of drug release, it can be used as an excipient in hydrophilic drug delivery system.

Thiol – functionalization of TSP

Thiol-functionalization of tamarind seed polysaccharide is done by esterification with thioglycolic acid. Thiol-functionalization is confirmed by SH stretch in Fourier-transformed infra-red spectra. The results of differential scanning colorimetry and X-ray diffraction study indicate increase in crystallinity [20].

Cynoethylation of TSP

The Cynoethylation of TSP is carried out in presence of acrylonitrile and sodium hydroxide under different reaction conditions. The cyanoethylated TSP exhibits non-Newtonian pseudoplastic behavior, relatively high viscosity, cold water solubility, and good solution stability and clarity, as compared to unmodified TSP [21].

Grafting of TSP

TSP has several drawbacks like uncontrolled rate of hydration, drop in viscosity on storage and susceptibility to microbial contamination. These disadvantages can be overcome by suitable grafting of TSP. Grafting is a method of modification in which monomers are covalently bonded onto the polymer chain and are grafted with synthetic polymer for the production of better natural products with less side effects and minimum loss of the inherent properties of the substrate. Grafting of gums with other polymers or ions requires availability of –COO– and/or –CH2OH groups in the gum. The main advantage of these grafted gums is that the resultant molecule can be tailored in such a way to yield a compound with the desired drug release profile. The grafted molecule could be selected in a way that it does not solubilize while the gum solubilizes at a particular pH. In this way, a predetermined drug release profile could be obtained [22].

Crosslinking of TSP

TSP can be cross-linked with epichlorhydrin which is one of the most significant method of modification of TSP. the cross-linking of TSP can be confirmed by FTIR. Cross-linked TSP was found to be more effective in retarding the drug release compared to unmodified TSP. For water-soluble drugs the release amount can also be controlled by partially cross linking the matrix. The extent of release can be varied by controlling degree of cross-linking. [23]. In another study, Aceclofenac-loaded chitosan-tamarind seed polysaccharide interpenetrating polymeric network microparticles were prepared by cross-linking TSP with chitosan and then preparing microparticles of this cross-linked product. The in vitro drug release studies from these aceclofenac-loaded chitosan-TSP IPN microparticles indicated a sustained release of aceclofenac over 8 hr following the Korsmeyer-Peppas model with anomalous (non-Fickian) diffusion drug release mechanism. The in vivo studies exhibited sustainedanti-inflammatory activity in carrageenan-induced rats over prolonged period after oral administrationof these newly developed aceclofenac-loaded IPN microparticles [24].

Copolymerization of TSP

β-Cyclodextrin–chitosan–glutaraldehyde terpolymers were synthesized by reacting variable weight fractions of β-cyclodextrin (β-CD) and chitosan (Chi), with a constant amount of crosslinker (glutaraldehyde).The equilibrium sorption properties of the copolymers investigated in aqueous solutions at pH 8.5 containing an organic anion (p-nitrophenolate; PNP) or an inorganic arsenate dianion ($HAsO_4^{2-}$) showed promising results which indicates that terpolymers can be an better alternative to surpass the disadvantages of native TSP [25].

PHARMACEUTICAL APPLICATIONS OF TSP AND ITS MODIFIED PRODUCTS

TSP is a usefull polymer for pharmaceutical use. Modification of TSP has more significant pharmaceutical value to this polymer. It is

used as a carrier for variety of drugs for preparation of controlled release formulations. Many techniques have been adopted to manufacture the TSP-based delivery systems which make it an exhilarating and promising excipient for the pharmaceutical industry for the present and future applications (Table 1).

Table 1: Pharmaceutical Applications of Tamarind seed Polysaccharide

Sr No.	*Formulation*	*Applications*	*Comments*	*References*
1	Aceclofenac loaded TSP-chitosan microparticles	As a drug release retardant	TSP-Chitosan cross-linked material can be used as sustained release component in gels	[24]
2	Nifedipine mucoadhesive tablet	As a mucoadhesive and sustained release component	More comfortable to the user to do less erosion, faster hydration rate, and optimum pH of surrounding medium	[26]
3	Salicylic acid, indomethacin, and Theophylline anhydrous tablets	Epichlorhydrin cross-linked TSP as drug release retardant	Controlling the degree of cross-linking of TSP can result in release kinetics that can be optimized to desire design.	[23]
4	In situ Gel Forming System	TSP is used a gelling agent.	TSP can be used to form in situ gel with sodium alginate and calcium carbonate.	[27]
5	Tablet granules associated with ZnSnanocrystals using TSP	Retarding the release of drug for upto 24 hr under accelerated conditions.	TSP embedded in ZnSnanocrystals were excellent drug release retardants	[28]
6	Metronidazole Mucoadhesive buccal Patches	As a mucoadhesive and sustained release component	TSP might be well utilized to develop a buccal drug delivery system with required mucoadhesive strength	[29]
7	Ketoprofen Diclofenac sodium	Assess the release behaviour of drugs, from cross linked tamarind seed polysaccharide	This study confirmed that the crosslinked TSP can be used as an effective release retardant and can be successfully used in commercial products.	[30]

Binder in tablet dosage form

Tamarind seed polysaccharide has been evaluated as a binder for tablet dosage forms for the wet granulation as well as direct compression methods because of its adhesive nature. The results indicated that tamarind seed polysaccharide could be used as binder for wet granulation and direct compression tableting methods [31]. Varying the amount of TSP in the tablet results in different types of release patterns of drug from the tablet

Mucoadhesive polymer

Mucoadhesion property of TSP has been improved by Derivatization with reagents bearing thiol functional groups. This improves the mucoadhesive and cohesive properties of the polymer. In a study by Kauret al, thiol-functionalization of tamarind seed polysaccharide was carried out by esterification with thioglycolic acid.Polymercompacts of thiolated tamarind seed polysaccharide was found to required 6.85-fold greater force to detachfrom the mucin coated membrane than that of native TSP. Higher mucoadhesion of gels containing thiolated TSP was achieved when comparative evaluation of Carbopol-based metronidazole gels containing thiolated TSP with gels containing native TSP for mucoadhesive strength using chicken ileum by modified balance method [20].

Sustained drug delivery

TSP possesses high drug holding capacity which was used to prolong the release of Verapamil hydrochloride. The release pattern was found to be analogous with matrices of other polysaccharide polymers such as ethyl cellulose, hydroxyethyl cellulose, and hydroxypropylmethyl cellulose, as well as the commercially available sustained release tablets [32]. Sustained release behavior of both water-soluble (acetaminophen, caffeine, theophylline and salicylic acid) and water-insoluble (Indomethacin) drugs on TSP was examined. Studies showed that cross-linked TSP is an excellent release retardant polymer for controlled release of both water-soluble and water-insoluble drugs. Zero-order release

can be achieved selecting sparingly soluble drugs such as indomethacin along with TSP [23]. For water-soluble drugs, the release amount can also be controlled by partially cross-linking the matrix. The extent of release can be varied by controlling the degree of cross-linking. The mechanism of release due to effect of diluents was found to be anomalous and was due to cross-linking [23]. Oral sustained release tablet was also prepared for 7-methoy deoxyVasicinone using TSP which showed promising results [36].

In-situ gel

In situ gel forming capacity of TSP was evaluated with and without sodium alginate. Results revealed that TSP was soluble in warm water while insoluble in cold water and in organic solvents. It was also exhibited that it can be used in dosage form, without any irritation. Results also showed that this polymer can be used to form in situ gel with sodium alginate [27].

Controlled Release Spheriods

In a study by Kulkarni GT et al it was found that TSP can beused as a release modifier for the preparation of diclofenac sodium spheroids, using extrusion spheronization technique. The effect of variables to arrive at spheroids with satisfactory particle shape, size and size-distribution was studied. The prepared spheroids were characterized for surface morphology, qualitative surface porosity, friability, bulk density, and flowproperties. The in vitro release studies exhibited a zero-order release kinetics that was confirmed by Higuchi's and Peppas' models. A good correlation was obtained among swelling index, viscosity, surface roughness of the polysaccharide, and in vitro dissolution profile of the spheroids. In the comparative bioavailability study, we found that the developed spheroids were able to sustain the drug release over 8 hr and could improve the extent of absorption and bioavailability of the drug [35].

Miscellaneous uses:

In a research by Pimple BP, et al it was found that TSP has a positive effect on the paracetamol induced hepatotoxicity in rats [37].

In Africa, TSP is used in Laxative, wound healing, abdominal pain, diarrhoea and dysentery, Helminth infections (parasitic worms) Fever and malaria [33].

It has also been used in water remediation. Researchers in the field of water treatment have reported good flocculation performance TSP for removal of various types of contaminants from water.

CONCLUSION

TSP is a promising natural polysaccharide that has many application in the pharmaceutical as well as food and textile industry. The versatility of this fantastic polysaccharide can be further used for the development of more novel and patient compliable drug delivery systems. The non-toxicity and cheaper availability along with non-carcinogenicity, mucoadhesivity, biocompatibility, high drug holding capacity and high thermal stability make TSP a very promising alternative over synthetic polymers. The research should be further carried out to explore the effectiveness of TSP as a better pharmaceutical excipient.

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