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REVIEW

Research Progress on Structure and Bioactivity of Longan Polysaccharide

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ABSTRACT

Longan originates from southern China and has high nutritional and health value. Recent phytochemistry and pharmacology studies have shown that polysaccharides are a main bioactive component of longan. Longan polysaccharides possess antioxidant, anti-aging, anti-tumor, immunomodulatory, and other bioactivities. Hot-water extraction, ethanol precipitation, and ultrasonic extraction are generally used to extract water-soluble longan polysaccharides. However, the relationship between the structure and bioactivity of longan polysaccharides remains unclear, requiring further investigation. The aim of this review is to evaluate the current literature focusing on the extraction, purification, structural characterization, and biological activity of longan polysaccharides. We believe that this review would provide a useful bibliography for further innovation and a basis for using longan polysaccharides in functional food.

KEYWORDS

Longan; polysaccharides; structural characterization; bioactivity

1 Introduction

Longan (*Dimocarpus longan* Lour.) is a valuable subtropical plant that is largely distributed in Southeast Asia, such as China, Vietnam, and Thailand [1]. The history of Longan in China is more than 2000 years. The plant has white flesh with a sugar content greater than 18%. It is rich in dietary fiber, vitamins, polysaccharides, and other substances needed by the human body. Longan has several medicinal values in traditional Chinese medicine, including spleen nourishment and strengthening, QI and blood replenishment, stomach strengthening, and muscle building [2]. In the ancient Chinese book "Qiminyaoshu," it is recorded that "longan was one puzzle, one flounder." The plant is also listed as an important tribute food in ancient times. The cultivation area and output of longan in China account for more than 50% of those in the world, and the general longan industry in China is in Guangdong Province. According to the China Food

Information Center Report in 2018, China's longan output was 2.03 million tons as of that year, and the harvest area was 288,000 hectares.

Modern research has found that longan can eliminate free radicals, reduce blood sugar, regulate the immune system, fight cancer, and promote intellectual development [3]. Numerous benefits of longan are derived from different chemical ingredients, such as polysaccharides, lipids, polyphenols, and flavonoids [4]. Recently, longan polysaccharide has attracted considerable attention because of its rich and diverse known biological activities, and it is a large class of bioactive components on the scientific network. Longan polysaccharide is attracting increasing research attention because it inhibits glycosylation reactions and possesses antioxidant, immunomodulatory, antitumor, and anti-inflammatory activities.

However, little is yet understood about the structure-activity relationship of longan polysaccharides. Hence, this review not only introduces the basic information about longan polysaccharides, but also comprehensively discusses and summarizes its structure-activity relationship. We believe this paper would provide a basis for future research as well as the innovation and application of longan polysaccharides in functional foods.

2 Extraction and Purification Methods

Although plant polysaccharides have a wide range of sources, all plant polysaccharides have similar extraction methods. The extraction process is the most critical step in the preparation of longan polysaccharides [5]. The choice of extraction method is influenced by the physical and chemical properties of the components as well as the extraction environment and interfering substances [6,7]. Currently, the research on the extraction process of longan polysaccharides is based on hot water extraction (Fig. 1), which is the simplest existing method. However, the method can only extract polysaccharides outside the plant cell wall, leading to the relatively low polysaccharide extraction rate and time wastage of the method. In a study [8] involving the extraction of longan polysaccharide by hot-water extraction combined with ethanol precipitation, the extraction temperature was 90°C, the reduced pressure concentration temperature was 65°C, and the finished polysaccharide was obtained after decolorization and drying with hydrogen peroxide. The extraction rate of longan polysaccharides was 3.41%. In another study involving the use of ultrasonic extraction [9] under the conditions of 120 W, 22 min, 60°C, and 241 W, 18 min, 51°C, longan polysaccharide had a higher recovery and 2, 2-diphenyl-1-picryl-hydrazyl-hydrate (DPPH) radical scavenging ability. The extraction temperature was 60°C, the ultrasonic power was 161.414 W, the extraction time was 31.111 min, the liquid material ratio was 19.9697, and the theoretical maximum extraction rate of polysaccharide was 19.96%. Here, the extraction rate of polysaccharides was higher than that of traditional hot-water extraction. These auxiliary extraction methods have been used for improving the extraction efficiency of longan polysaccharides, shortening the extraction time, and reducing material waste [10].

Crude polysaccharide extracts typically contain large amounts of protein [11], and the proteins must be removed by an appropriate process to improve the purity of polysaccharide products [7,12]. The Sevag method and trichloroacetic acid method are generally used to deproteinize crude polysaccharides [13]. Decolorization was performed with hydrogen peroxide before further purification by ion exchange chromatography, and gel filtration chromatography was performed. The semi-pure longan polysaccharides were fractionated and purified by DEAE cellulose column chromatography, and then the polysaccharide fractions were further separated and purified by the Sephadex G-100 column. Finally, UV scanning and Sephadex G-100 column chromatography were used. Wang et al. used a DEAE cellulose column to elute with a flow rate of 0.5 mL/min, and two symmetrical peaks, Lps-1 and Lps-2, appeared on the elution curve. Both peaks were eluted in the linear elution process of NaCl, indicating that longan polysaccharide is an acidic heteropolysaccharide without neutral sugar [8]. The Sephadex G-100 column chromatography was then performed. The results showed that Lps-1 separated two components—Lps-1-A and Lps-1-B—while

Lps-2 only washed out a single peak, indicating that Lps-2 was relatively pure. In addition, a small protein elution peak was also detected in the range of the Lps-2 elution curve, further indicating that Lps-2 was a sugar protein complex [14].

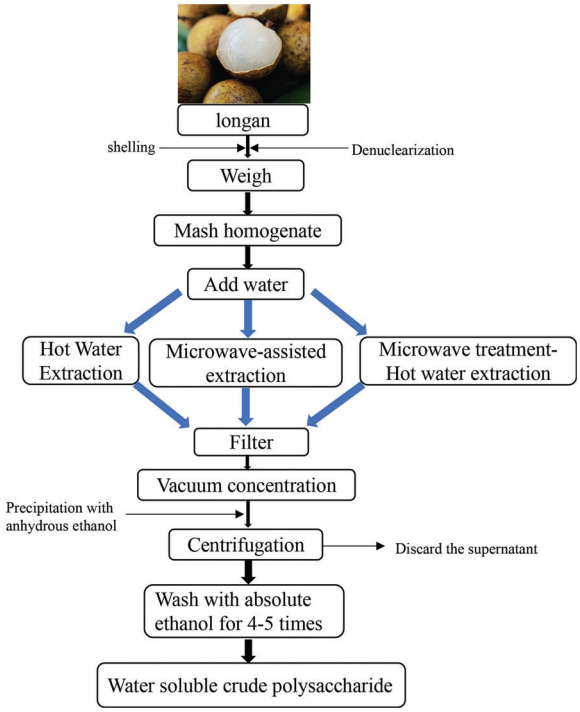

Figure 1: Extraction process of longan polysaccharides

This paper reviews the purification and separation methods of longan polysaccharides. The crude extraction of longan polysaccharide was performed by ultrasonic-assisted extraction, and the purified longan polysaccharide was obtained after protein removal, decolorization, ethanol precipitation, centrifugation, and freeze-drying, DEAE cellulose column chromatography, filtration, Sephadex G-100 column chromatography, dialysis, and freeze-drying [15,16] were also performed.

3 Physiochemical and Structural Features of Longan Polysaccharides

The main aspects of the physicochemical and structural characteristics of plant polysaccharides are the monosaccharide composition, molecular weight, sequence of monosaccharides, configuration of glycosidic bonds, types of glycosidic bonds, and positions of glycosidic bonds [17,18]. Many studies have separated various monosaccharides and chemical structures from longan fruits [19].

3.1 Monosaccharide Compositions

Glycosidic bond hydrolysis, derivatization, gas chromatography (GC), and high-performance liquid chromatography (HPLC) detection are often used to quantify monosaccharide compositions [20]. Owing to the variety of extraction and purification processes, detected monosaccharides also differ but are mainly composed of rhamnose, xylose, arabinose, and galactose in different proportions [21]. Han separated two kinds of polysaccharides (FLP and DLP) from fresh longan and dry longan and found that DLP was composed of rhamnose, mannose, glucose, and galactose in a molar ratio of 2.0:1.0:1.0:10.5, with an average molecular weight of 1.06×10^7 g/mol; similarly, FLP was composed of mannose and glucose with a

molar ratio of 0.59:1 and an average molecular weight of 1.31×10^7 g/mol. Different kinds of longan polysaccharides might have different monosaccharide compositions and molar ratios. More monosaccharides can also be found in the future through advances in scientific and technological development [22].

3.2 Average Molecular Weights

Several studies on longan polysaccharides have determined the average molecular weight of polysaccharides using HPLC and high-performance gel permeation chromatography [23]. Yang et al. [24] used gel permeation chromatography to determine the molecular weight of longan polysaccharide (PLFB) to be 4.2×10^5 Da. In various studies, the average molecular weight of longan has been in the approximate range of 10^4–10^7 Da.

3.3 Chemical Structures

Only a few studies have investigated the chemical structure of longan polysaccharides. In a study [9]. Longan polysaccharide (PLFP) was extracted from different longan peels by hot water extraction. By removing the protein and conducting analyses by gas chromatograph, it was found that the monosaccharide composition was composed of L-arabinofuranose (32.8%), D-glucopyranose (17.6%), D-galactopyranose (33.7%), and D-galacturonic acid (15.9%). The analysis results showed that the backbone consisted of →5)-L-Ara*f*-(1→, →6)-D-Glc*p*-(1→, →3)-D-Gal*p*-(1→, →3)-D-Gal*p*A-(1→ and →6)-D-Gal*p*-(1→ with a molar proportion of 2:1:1:1:1.

Longan pulp polysaccharide was extracted using hot water (LP-H), superfine grinding (LP-S), and superfine grinding-assisted enzymatic treatments (LP-SE). All three LPs contained similar glycosidic linkage of →3)-α-L-Ara*f*-(1→, →3, 6)-*β*-D-Gal*p*-(1→, and α-L-Rha*p*-(l→, whereas they each contained specific glycosidic linkage of →4)-*β*-D-Glc*p*-(l→, →4)-*β*-D-Gal*p*-(1→, and →5)-α-L-Ara*f*-(1→ in LP-H, LP-S, and LP-SE, respectively [14].

4 Biological Activities

Longan polysaccharide research and analyses have provided insight into their antioxidant, immunomodulatory, antitumor, anti-inflammatory, and anti-glycated activities [25,26].

4.1 Antioxidant Activity

Natural substances are important sources of antioxidants, and many polysaccharides have antioxidant activity [27,28]. Antioxidant activity is an important index for detecting plant polysaccharides [29,30]. Many studies have verified the antioxidant activity of longan polysaccharides. Yang et al. studied the antioxidant substances in longan. Under the condition of microwave-assisted extraction, the scavenging rates of DPHH free radical and hydroxyl free radical of longan polysaccharide were 62.45% and 54.36%, respectively [24]. Jiang et al. used the DPPH free-radical scavenging method to detect the free radical scavenging activities of crude longan polysaccharide (LSP), extracted macromolecular longan polysaccharide (LSP1), and small-molecule longan polysaccharide (LSP2) [31]. When the concentration of longan polysaccharide (LSP) reached 700 (g/mL), the scavenging activity of DPPH radical increased with the increasing concentration of longan polysaccharide (LSP), whereas (LSP3) showed a lower antioxidant activity than that of (LSP1) and (LSP2). This result is similar to the previous report that crude polysaccharides have a better antioxidant effect than purified polysaccharides. The relationship between the structural characteristics of polysaccharides and antioxidant activity remains unclear [32].

4.2 Immunomodulatory Activity

Natural active polysaccharides can participate in various immune responses [33]. Mental stress can directly affect the immune state of the body through the pituitary thymus axis, and long-term mental

stress leads to a decline in human immune function [34,35]. Therefore, immune regulation is important. Rong et al. [36] isolated longan polysaccharides (LPD2) from longan pulp, and the effect of (LPD2) on macrophage phagocytosis was determined. LPD2 at 6.25–50 μg/mL enhanced phagocytosis in a dose-dependent manner ($P < 0.05$). Meanwhile, the effect of LPD2 on macrophage phagocytosis was not inhibited by PMB ($P > 0.05$). The use of a 50 μg/mL LPD2 treatment increased phagocytosis to 205.1 ± 9.3% of the control group, indicating that LPD2 significantly enhanced the phagocytic activity of macrophages. Tong et al. [37,38] found that longan polysaccharide enhanced the phagocytosis of macrophages; when the polysaccharide concentration was 100–400 μm/mL, macrophage phagocytosis was negatively correlated with polysaccharide concentration [20]. Longan polysaccharide influences immune activity, and different processing methods have varying effects on the immunoregulatory activity of longan polysaccharides (Fig. 2) [39].

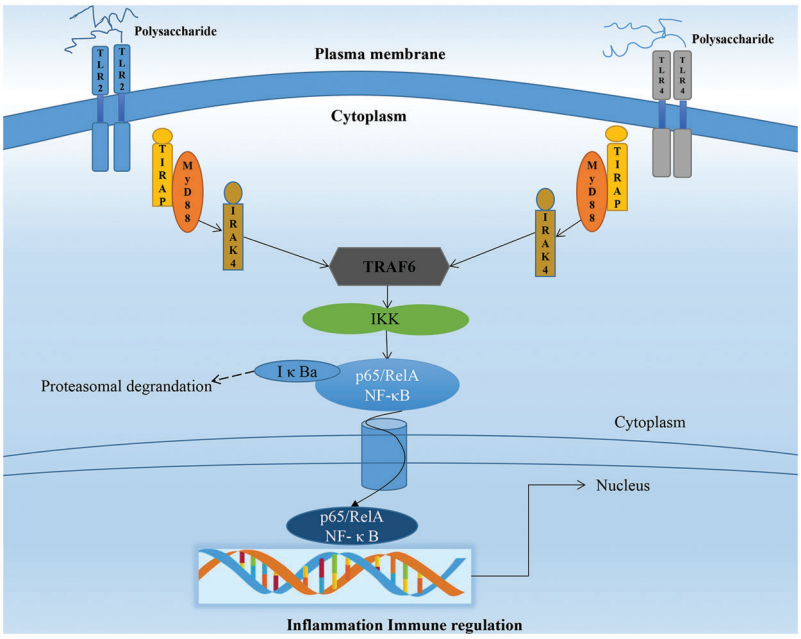

Figure 2: Possible molecular mechanism of (LPD2) activating macrophages

4.3 Antitumor Activity

The antitumor mechanism of polysaccharides can be divided into two categories: first, it improves the immune function of the body by activating the immune system, activating lymphocytes and macrophages, promoting cytokine secretion, and activating complement, as well as by indirectly playing an antitumor role. Second, it affects the growth cycle, ultrastructure, signal transduction pathway in tumor cells, and biochemical characteristics of the tumor cell membrane [40,41]. Zhong et al. [42] used longan polysaccharide (UELP) prepared by the ultrasonic extraction process to conduct *in vivo* tumor inhibition and *in vivo* immune experiments on S180 tumor-bearing mice. The results showed that UELP significantly enhanced the delayed type allergy and phagocytosis of peritoneal macrophages, considerably enhancing the proliferation of splenic lymphocytes. The *in vivo* tumor inhibition results also showed that UELP had a strong S180 tumor inhibition effect, and the highest tumor inhibition rate was 95.08%. The *in vitro* antitumor experiment showed that longan chitosan inhibited the growth of tumor cells BELE-7404, SKVO3, and MCF-7, as well as an antitumor effect [43].

4.4 Anti-Inflammatory Activity

Polysaccharides with anti-inflammatory effects can regulate one or more inflammatory mediators secreted by inflammatory cells, balance the levels of pro-inflammatory factors and anti-inflammatory factors in inflammatory sites, and affect all stages of inflammation development [44]. Chen et al. [45] conducted a study using *Euphoria longan Steud* (Lour.) as a fruit and traditional Chinese medicine with the function of anti-inflammatory and immune regulation. The results of inflammatory responses induced by middle cerebral artery occlusion in rats were published. Compared with the model group, polysaccharides of *E. longan Steud* (Lour.) reduced the neurological function score, brain water content, infarct volume, myeloperoxidase (MPO) activity, tumor necrosis factor-α (TNF-α), and interleukin-1β (IL-1β) level. Polysaccharides of *E. longan Steud* (Lour.) had a protective effect on cerebral ischemia/reperfusion injury, and the mechanism might be related to the reduction of MPO TNF-α and IL-1β mediated inflammatory response in the brain [45].

4.5 Anti-Glycosylation

Glycosylation refers to the combination of the amino group of protein and the aldehyde group of sugar [46]. The first stage of the non-enzymatic reaction of proteins with glucose yields bases and products, which undergo oxidation and molecular rearrangements into irreversible glycosylation products. Yang et al. [47] demonstrated the inhibitory effect of longan polysaccharide (PLFP) on the formation of advanced glycation end products. Longan polysaccharide and aminoguanidine with the same concentration (0.5 mg/mL) had higher anti-glycation activity than that of aminoguanidine in four weeks. The differences between PLFP and aminoguanidine might be due to their inhibition mechanism. The anti-glycosylation activity of PLFP is likely due to its antioxidant activity and the existence of a special structure. Therefore, further studies are necessary to better understand the structure and anti-glycosylation activity of longan polysaccharides.

5 Correlation of Structure, Content, and Biological Activity

The bioactivity of polysaccharides is closely related to their chemical composition and structures [48–50]. However, no clear relationship between the activity and structure of longan polysaccharides has been identified [51,52], leaving room for speculation.

The chemical structure of polysaccharides has a considerable impact on their biological activities [53]. Table 1 summarized the main structural characteristics of longan polysaccharides, such as molecular weight, monosaccharide composition, chemical structure, and biological activity. For example, fresh longan polysaccharides (FLP) and air-dried longan polysaccharides (DLP) have been used as raw materials for structural and immunomodulatory activity comparisons. The ratio of 1, 3 chain residues of longan polysaccharides may increase during the drying process and have a greater impact on the immunomodulatory activity of longan polysaccharides [54,55]. The effects of alkali dissociation on the immune regulation of longan polysaccharide (LPI) can significantly enhance the proliferation of splenocytes and cytotoxicity of NK cells due to its micro-dissociated spherical conformation or single helix chain [56]. The results showed that the single helix chain could play an important role in the activation of lymphocytes and NK cells.

Table 1: Polysaccharides isolated from longan fruit pulp (Longyan)

No.	Compound name	Molecular weight	Monosaccharide composition	Structures	Biological activities	Reference
1	LPS-N	1.38×10^4 Da	Xyl and Glc in ratio of 1:1.9		Anti-inflammatory	[3]
2	PLFB	4.2×10^5 Da	Ara, Glc, Gal, and GalA in the ratio of 3.28:1.76:3.37:1.59	Backbone consisted of →5)-L-Ara*f*-(1→, →6)-D-Glc*p*-(1→, →3)-D-Gal*p*-(1→, →3)-D-Gal*p*A-(1→ and →6)-D-Gal*p*-(1→	Anti-glycated	[9]
3	LP-2	1.08×10^5 Da	Glc	Backbone composed of *β*-(1→6)-linked-Glc*p*	Antioxidant	[10]
4	LPIIa	1.593×10^5 Da	Rha, Ara, Xyl, Man, Glc, and Gal	Backbone composed of (1→3,4)-linked-α-Rha*p*, (1→4)-linked-*β*-Gal*p*, (1→6)-linked-*β*-Gal*p* and (1→3,6)-linked-*β*-Gal*p*	Anti-inflammatory	[11]
5	ASPs I		Xyl, Ara, Glc, and Gal	Composed of →3)-Xyl*p*-(1→ and →3, 4)-Xyl*p*-(1→	Immunomodulation	[12]
6	LP1	1.1×10^5 Da	Glc, GalA, Ara, and Gal in the ratio of 5.39:1.04:0.74:0.21	Backbone of →4)-α-D-Glc*p*-(1→4)-α-D-Gal*p*A-(1→4)-α-D-Glc*p*-(1→4)-*β*-D-Glc*p*-(1→, side chains composed of →2)-*β*-D-Fru*f*-(1→2)-L-sorbose-(1→ attached to the *O*-6 position of the α-D-Glc*p*	Antitumor agent	[13]
7	LP-H LP-S LP-SE	2.38×10^5 Da 2.28×10^5 Da 1.90×10^5 Da	Rha, Ara, Man, Glc, and Gal	Glycosidic linkage of →4)-*β*-D-Glc*p*-(l→ Glycosidic linkage of →4)-*β*-D-Gal*p*-(1→ Glycosidic linkage of →5)-α-L-Ara*f*-(1→	Cell proliferation	[14]
8	LPg1 LPx1	1.06×10^7 Da 1.31×10^7 Da	Rha, Man, Glc, and Gal in the ratio of 0.2:0.21:1:0.2 Man and Glc in the ratio of 0.59:1		Immunomodulation	[16]
9	LYRP2	1.1×10^5 Da	Glc	Main chain *β*-D-(1→3)-Glc*p*, and branches with *β*-D-(1→3)-Glc*p*-*β*-D-→1)-Glc*p* and *β*-D-(1→4)-Glc*p*-*β*-D-1)-Glc*p* in which 1-linked Glc*p* terminal residues	Immunomodulation Antitumor	[17]

(Continued)

Table 1 (continued)

No.	Compound name	Molecular weight	Monosaccharide composition	Structures	Biological activities	Reference
10	LSP		Ara, Gal, Glc, and Man	Major components of →6)-Gal*p*-(→1, Glc*p*-(→1 and →6)-Glc*p*-(1→ glycosidic linkages	Antioxidant	[31]
11	LYP2		Glc, Ara, and GalA, sorbose in ratio of 5.39:1.04:0.74:0.21	Composed of →4)-α-D-Glc*p*-(1→4)-α-D-Gal*p*A-(1→4)-α-D-Glc*p*-(1→4)-*β*-D-Glc*p*-(1→ and branches with →2)-*β*-D-Fru*f*-(1→2)-L-sorbose-(1→, which was (1→6)-linked to α-D-Glc*p*	Immunomodulation Antioxidant	[35]
12	LPD2	9.64×10^6 Da	Ara, Man, Glc, and Gal in the ratio of 0.25:0.49:1:0.5	Backbone composed of (1→4)-*β*-Glc*p* and (1→6)-*β*-Man*p*.	Immunomodulation	[36]
13	LPIa	1.47×10^5 Da	Rha, Rib, Ara, Xyl, Man, Glc, and Gal in the ratio of 0.99:1.37: 34.61:1.48:1.73: 5.86:55.16	Composed of→3)-α-Ara*f*-(1→, →3, 6)-*β*-Gal*p*-(1→, α-Ara*f*-(1→ and →5)-α-Ara*f*-(1→	Immunomodulation	[43]
14	FLP	1.31×10^7 Da	Man and Glc in the ratio of 0.59:1	Composed of →6)-α-D-Glc*p*-(1→	Immunomodulation	[57]
	DLP	1.06×10^7 Da	Rha, Man, Glc, and Gal in the ratio of 0.2:0.21:1:0.2	Composed of →6)-α-D-Glc*p*-(1→, →3)-*β*-D-Glc*p*-(1→, →3)-*β*-D-Gal*p*-(1→ and →3)-α-L-Rha*p*-(1→	Cell proliferation	

6 Conclusions and Views

Longan polysaccharides can be effectively extracted by ultrasonic and hot-water extraction and ethanol precipitation, which has a better effect than that of simple hot-water extraction. Longan polysaccharides possess important biological activities, including antioxidation, immune regulation, antitumor, anti-inflammatory, and anti-glycosylation activities. Recently, scientific researchers have extensively investigated the extraction, structures, and biological activity of longan polysaccharides. However, the structure of longan polysaccharides is diverse and complex, and the relationships between the biological activity and chemical structure of polysaccharides are not clear, creating the need for further exploration. Thus, in-depth research in this area is needed to understand the functions of longan polysaccharides more comprehensively. Moreover, as the research on longan polysaccharides has been accelerated recently, further *in vivo* animal research and clinical experiments are required to determine the impact of longan polysaccharides on the human body.

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Conflicts of Interest: The authors declare they have no conflicts of interest to report regarding the present study.

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