Production of Chrome-Free Tanning Agents from Agricultural Waste: Valorization of Longan Seed

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Waste: Valorization of Longan Seed

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Abstract

Global longan production in 2023 reached 4.2 million tonnes, with China contributing 60%. The seed, about 17% of fruit mass, is mostly discarded or burned, wasting biomass and polluting soil and air. Converting seed polysaccharides into tanning agents offers a waste-minimising, chrome-free alternative. Native polysaccharides are poorly soluble and show limited collagen affinity; fragments of 500–3000 Da crosslink optimally, while smaller or larger molecules act as fillers. Controlled depolymerisation and modification are therefore essential. In this study, longan seeds were treated with á-amylase-assisted ultrasonic hot-water extraction to yield a high-purity polysaccharide (LSP) rich in vicinal diols. Compared with the non-enzymatic control, the enzymatic route increased yields of total sugars, polyphenols, saponins and reducing ends. LSP was selectively oxidised with NaIO4 at varying stoichiometries to produce dialdehyde longan seed polysaccharide (DLSP). Moderate oxidant levels cleaved glycosidic bonds and converted C2-C3 diols into aldehyde groups; excess periodate over-oxidised aldehydes to carboxylates, decreasing active carbonyl content. The resulting lowmolecular-weight DLSP, bearing high densities of aldehyde and hydroxyl groups, rapidly penetrated collagen fibres and formed stable cross-links. Leather tanned with the optimised DLSP exhibited a shrinkage temperature of 76.4 °C, tensile strength of 17.03 MPa, elongation at break of 90.59% and tear strength of 86.54 N/mm, outperforming formaldehyde- and

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glutaraldehyde-tanned controls. This work demonstrates that á-amylase-coupled ultrasonic extraction efficiently releases polysaccharides, polyphenols and saponins from longan seeds; selective periodate oxidation converts these extracts into a novel, biodegradable, chromium-free tanning agent, providing a sustainable alternative for the leather industry and valorising agro-waste.

Key words: Longan seed; sodium periodate; dialdehyde polysaccharide; chromium-free tanning agent

1. Introduction

Longan (Dimocarpus longan Lour.), a member of the Sapindaceae family and the genus Dimocarpus, is widely cultivated across tropical and subtropical regions and gains high consumer popularity. In 2023, global longan production reached approximately 4.2 million tons[1], with China accounting for 60% of the total[2]. Longan seeds account for approximately 17% of the fresh weight of the whole fruit[3]. However, they are usually discarded as waste or incinerated for energy recovery during fruit processing. Such low-value disposal methods not only squander a substantial quantity of premium lignocellulosic biomass but also aggravate soil and atmospheric pollution, making the valorisation of longan seeds imperative. Given their chemical composition, longan seed extracts are prospective precursors for bio-based tanning agents. To date, however, no study has explored the enzymatic hydrolysis of longan seeds to produce low-molecular-weight polysaccharides that can serve as chrome-free tanning precursors.

Sodium periodate (NaIO4) is a highly selective oxidant that converts the vicinal-diol moieties at C-2 and C-3 of polysaccharides into aldehyde functionalities, yielding dialdehyde polysaccharides[4]. The iodine-containing waste stream can be regenerated with hypochlorite or ozone and recycled for subsequent dialdehyde-polysaccharide production. The introduction of aldehyde groups into the tanning agent enables

nucleophilic addition to the amino and imino groups of basic amino acid residues in proteins, generating covalent cross-links[5]. Periodate-mediated oxidation of polysaccharides for chrome-free tanning has thus become one of the most intensively investigated research directions in biomass-based green tanning research.

2. Methodology

2.1 Preparation of LSP

Longan seeds were obtained by manually separating the pericarp and pulp from the fruit. After washing and ovendrying, hydrophilic extracts were prepared by ultrasoundassisted hot-water extraction with or without enzyme[6]. Briefly, longan-seed powder (100 g) was suspended in 400 mL of α-amylase solution (5 U/mL) and incubated at 65°C for 8 h under constant agitation (60 rpm). The mixture was then subjected to ultrasonic treatment (40 kHz, 400 W) for 30 min. The resulting slurry was centrifuged at 5,000 rpm for 10 min at 4°C; the supernatant was concentrated at 65°C and de-pigmented by vacuum solid-phase extraction using activated carbon as sorbent. Finally, the clarified extract was lyophilised at -58°C and 15 Pa for 72 h in a freeze-dryer (Boyikang Laboratory Instruments Co., Ltd., Beijing, China).

2.2 Preparation of DLSP

10.0 g of LSP were dispersed in 150 mL of deionised water and completely dissolved. Sodium periodate was then added at mass ratios (LSP:$NaIO_4$) of 1:0.25, 1:0.5, 1:1, 1:1.5 and 1:2, and the mixtures were stirred continuously at 25 °C in the dark for 24 h. The oxidation was quenched by adding ethylene glycol under stirring; the solutions were filtered, and the DLSP-containing filtrates were lyophilised to yield powdered samples[7].

2.3 Evaluation of Tanning Efficacy

Add water at a dosage of 800% on the weight of pickled sheepskins (the same below) and sodium chloride at 30 g/ L on the volume of water (the same below) into the drum, and run the drum at 35 °C and 18 rpm for 10 min. Place a piece of pickled sheepskin into the drum, followed by tanning with 15 g/L DLSP (concentration calculated on a solid content basis) for 4 h. Subsequently, adjust the pH value of the tanning liquor from 2.5–2.8 to 7.8–8.0 using 15 g/L sodium bicarbonate. To ensure sufficient crosslinking between DLSP and collagen chains, keep the drum running for another 4 h and then let it stand for 12 h. Drain the tanning liquor, add water at 1000% on the weight of pickled sheepskins, and operate the drum at room temperature for 30 min to wash the tanned sheepskins. After draining the washing liquor, add water at 300% on the weight of pickled sheepskins, 100 g/L Lubricating HighPerformance Fatliquor (LHP) and 20 g/L General HighLubricity Fatliquor (GHL) into the drum, and run it at 50 °C for 2 h. Adjust the pH value to 3.5–3.7 in six separate additions with diluted formic acid solution, and continue running the drum for an additional 30 min. Drain the fatliquoring liquor, add water at 1000% on the weight of pickled sheepskins, and run the drum at room temperature for 30 min. Finally, air-dry the leather indoors[8].

3. Result & Discussion

As the $NaIO_4$ dosage increased from 1:0.25 to 1:1 (w/w, $NaIO_4$:LSP), the shrinkage temperature (Ts) of sheepskins tanned with hot-water-extracted DLSP rose markedly, a trend broadly consistent with the findings of Zhu et al.[9]. Leather treated with αA-DLSP(1:0.5) attained a Ts of 76.4 °C, significantly higher than that of any other DLSP group ($P < 0.01$). Ts exhibited an initial increase followed by a decline, an observation attributable to concurrent changes in aldehyde content and molecular size. Elevated aldehyde density and reactivity promote extensive inter-fibrillar cross-linking that stabilises the collagen matrix and amplifies tanning efficacy. Lowmolecular-weight tannins readily penetrate and cross-link the fine architecture of the pelt; however, excessively small

fragments fail to establish durable bridges between collagen fibres[7]. Consequently, DLSP combining an optimal molecular weight with high aldehyde content and reactivity is expected to deliver superior tanning performance.

The active carboxyl groups of DLSP can, in principle, form stable amide bonds with the amino moieties of collagen via covalent cross-linking[10,11], thereby reinforcing the structural integrity of the leather. However, the low reaction temperature and the absence of a catalyst restrict the extent of this pathway, so only a minor fraction of the carboxyl functionalities actually participate. Consequently, the outstanding tanning performance of DLSP is primarily ascribed to imine condensation between aldehyde and amino groups, augmented by synergistic hydrogen-bonding and electrostatic interactions contributed by hydroxyl and carboxyl residues. The results further demonstrate that DLSP combining an optimal molecular weight with high aldehyde content and reactivity affords the most efficient tannage. In addition, the resulting leathers exhibit favourable physical properties, indicating that DLSP is a promising candidate to replace conventional tanning agents and offers the leather industry a novel, sustainable process option.

4. Conclusion

Using enzymatic extraction combined with ultrasonic assistance to extract LSP is a green and sustainable technology. LSP is rich in vicinal-diol structures that can be selectively oxidised by $NaIO_4$. Upon $NaIO_4$-mediated oxidation, the glycosidic linkages of LSP are cleaved and the vicinal diols are converted into aldehyde functionalities, yielding DLSP. Evaluation of the physical–mechanical properties of the resulting leathers revealed that molecular weight and the activity/content of functional groups (aldehyde, carboxyl, and hydroxyl) are the principal factors governing tanning efficacy. DLSP fractions of lower molecular weight and higher aldehyde content/reactivity penetrate and react more readily within the hierarchical architecture of collagen fibres, resulting in a higher shrinkage temperature of the leather.

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