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β-MANNAN-OLIGOSACCHARIDES: A REVIEW

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ABSTRACT

Mannan-oligosaccharides (MOS) have gained significant attention as prebiotics from yeast, particularly for their use in animal feed and dietary supplements. However, a promising method for obtaining MOS prebiotics involves converting lignocellulosic biomass derived from plant materials, agricultural, agro-industrial, and forestry residues, which are known as β-MOS. This work provides a review of the potential extraction techniques of β-MOS, and possible applications, emphasizing their numerous health benefits. This review covers several aspects of β-MOS production, including the types of mannans, pretreatment methods, hydrolysis processes utilizing organic and inorganic acids, alkalis, and enzymes, as well as non-conventional methods for obtaining MOS. Additionally, it discusses the techniques for MOS purification and their applications in enhancing health and nutrition.

Keywords: Hydrolysis. β-MOS. Prebiotics. Bioproducts Engineering, Waste valorization

1 INTRODUCTION

The global prebiotic ingredients market has experienced remarkable growth, rising from $5.81 billion in 2022 to $6.47 billion in 2023, with a compound annual growth rate (CAGR) of 11.4%. The market is projected to reach $9.7 billion by 2027, with a CAGR of 10.6%.[1] In recent years, an increasingly popular method of obtaining prebiotics has been the conversion of lignocellulosic biomass from agricultural, food, and forestry wastes.[2] Ongoing efforts span a spectrum of sources for prebiotic production, including xylan-based xylo-oligosaccharides (XOS), galactan-based galacto-oligosacharides (GOS) arabinan-based arabino-oligosaccharides (AOS), and mannan-based mannan-oligosaccharides (MOS), with a focus on determining production feasibility.[3]Despite the significant growth of the prebiotics market, there is a strong interest in the use of lignocellulosic biomass due to its abundance and cost-effectiveness. In this context, the extraction of oligosaccharides from lignocellulosic biomass is in line with evolving bioeconomy models.[4] However, the existing literature predominantly focuses on α-MOS production from yeast, with limited discourse on β-MOS, despite its potential. Therefore, this review aims to comprehensively outline the technical methodologies for β-MOS production from lignocellulosic biomass and plant sources, considering the structural characteristics of the primary mannans in the feedstock. The review covers the entire production process, from pretreatment to purification, and highlights potential applications of MOS from vegetal sources, emphasizing the associated health benefits.

2 MATERIAL & METHODS

Google Scholar, Web of Science, PubMed, and other academic databases were utilized to identify relevant studies in English, Portuguese, and Spanish. Specific terms and thesauri related to MOS were employed, including "Mannan-Oligosaccharides (MOS)", "β-MOS", "oligosaccharides derived from mannans", "lignocellulosic biomass", "plant sources", "biomass hydrolysis", prebiotics" and other similar words. These keywords were combined using Boolean operators (AND, OR) to refine searches and ensure the inclusion of all pertinent articles. Studies addressing the extraction, purification, and applications of MOS, particularly β-MOS derived from plant sources, lignocellulosic biomass, and agro-industrial residues, were included. After the initial search, all relevant articles were collected, and duplicates were removed. Key data were extracted from each study, including types of mannans, pre-treatment techniques, conventional and unconventional hydrolysis methodologies, purification alternatives, and applications of MOS, categorized by mannan type according to the source.

3 RESULTS & DISCUSSION

Lignocellulosic biomass, comprising cellulose, hemicellulose, and lignin, is vital for industrial applications.[5] Hemicellulose, constituting 15-25% of dry lignocellulose mass, varies in abundance across plant species and tissues, containing monosaccharide units like D-xylose, D-mannose, and D-arabinose.[6] Mannans, classified into linear mannan, glucomannan, galactomannan, and galactoglucomannan, contribute to cell wall strength, with variations in structural composition and properties.[7] Linear mannan comprises β-1,4-glucosidic bonds and is typically insoluble in cold water.[8] Glucomannan, characterized by a mannose:glucose ratio, exhibits viscosity and solubility, varying across sources.[9] Galactomannans feature galactose-substituted mannose chains, influencing water retention in seeds under high temperatures.[7] Galactoglucomannan (G-Gl), found in hardwoods and softwoods, combines glucomannans and D-galactose with acetylated mannose residues.[9] Hardwoods contain 3-5% mannan, while softwoods have higher content, ranging from 15-20%.[10] Various raw materials exhibit different mannan contents based on their type. For linear mannan, Palm Kernel Cake (PKC) contains 35.2%[11], Ivory Nut has the highest content at 86%[12], and Açaí Seed contains 53.8%[13]. In terms of glucomannan, *Eucalyptus grandis* has 0.8%[14], while Konjac tuber contains 8-10%[15]. For galactomannan, Copra Meal (CM) contains 61%[16], Locust Bean Gum (LBG) has 85.2% [17], Spent Coffee Ground (SCG) contains 39.3%[18], *Sesbania*

Virgata has 94.8%[19], and *Geditsia Sinensis* has 47-52%[20]. Additionally, Pine wood contains 15.79% glucomannan [21], and Bagasse contains 1.5-3.4% glucomannan[22,23]. These materials, particularly those rich in linear mannan and galactomannan, are potential for oligosaccharide production like MOS, due to their high mannan content.

The utilization of pretreatments for mannan-rich materials is of paramount importance for the facilitation of enzymatic hydrolysis and the improvement of the efficiency of MOS production. Steam explosion is a widely utilized method, typically involving the application of high-pressure steam at temperatures ranging from 150°C to 210°C, with times varying based on the specific type of mannan. For linear mannans and galactomannans, temperatures of approximately 190°C to 210°C for 15 minutes are most effective, but for G-Gl, is required longer exposure times, ranging from 30 to 90 minutes.[14]Additionally, autohydrolysis has been documented in the literature, particularly for wood, with temperatures between 150°C and 200°C for 30 minutes.[25] Alkaline pretreatment, which employs agents such as NaOH is an effective means of breaking down lignin and enhancing hydrolysis rates. Typical conditions for this process involve NaOH concentrations ranging from 0.5 to 2.5 N, temperatures between 50°C and 121°C, and reaction times of up to six hours. This method appears to be particularly effective for galactomannans, yielding better results than untreated or acid-pretreated.[26] The use of dilute acid conditions, such as 0.1% to 5% sulfuric acid at temperatures between 100°C and 145°C for limited times, has been demonstrated to maximize MOS yields while minimizing by-product formation.[27]

Enzymatic hydrolysis, although slower than conventional methods, is highly effective for obtaining MOS by breaking glycosidic bonds in mannan polysaccharides.[9]The primary enzyme responsible is β-mannanase, which cleaves β-(1→4) glycosidic bonds in mannan-rich materials.[5] β-mannanase operates through a double displacement reaction mechanism, forming an oligosaccharide-enzyme complex that releases smaller oligosaccharides[28] Fungal acidic β-mannanases, especially from the Aspergillus genus, exhibit optimal activity at pH values ≤ 6.[29] Bacterial β-mannanases, often produced by bacilli, are notable for their salt tolerance, pH stability, and thermostability.[3] MOS yield is significantly influenced by pretreatments, which enhance enzymatic degradability and facilitate enzyme access to the polymer backbone.[30] In mannan degradation, β-mannanases also can work with other enzymes like β-mannosidase, which hydrolyzes β-1,4-linkages at the non-reducing ends of mannans, releasing mannose.[31] Additionally, β-glucosidases break down 1,4-β-D-glucopyranose in glucomannans and galactoglucomannans.[32] α-Galactosidase and acetyl mannan esterases remove galactose and acetyl groups, enhancing hydrolysis through homo- and hetero-synergistic interactions among these enzymes.[28]

A variety of acid hydrolysis extraction processes have been evaluated for the direct production of MOS using different types of organic and inorganic acids. Among inorganic acids, sulfuric acid is a commonly used acid to produce MOS with concentrations ranging from 0.1% to 5%, temperatures between 60 and 121°C, and times from 5 minutes to 12 hours.[27,33,34] For galactomannans, reactions should not exceed 30 minutes at concentrations above 2% to avoid monomeric sugar production. Furthermore, the recommended inorganic acid concentration for obtaining oligosaccharides is 1%, since at lower concentrations the small conversion rate favors the limitations of acid mass transfer, hinders the decomposition of the polymer into its monomeric form.[33] Organic acids, such as citric acid[33] and acetic acid [35], have also been employed for MOS extraction. Acetic acid has been demonstrated to yield superior results due to its weaker dissociation constant, allowing for higher concentrations up to 5M. The use of milder conditions, such as 0.05 M acetic acid with ferrous chloride, also results in satisfactory hydrolysis yields of approximately 50% from galactomannans. [35]

The use of alkali for extracting MOS is less documented compared to acid hydrolysis. Bello et al. (2018) demonstrated that using 2% NaOH at 40°C for 1 hour on defatted PKC resulted in a hydrolysis yield of 8.73%, with a mannose-rich content of 38.86%.[36] While limited as a main method for plant material, alkali treatment is more commonly used as a pretreatment to purify mannans, as shown by Gibril et al. (2020), who extracted mannans from *Hyphaene Thebaica* seeds using NaOH concentrations of 0.05-0.3 N at 30-90°C for 30-120 minutes, achieving yields over 90%.[37]

Non-conventional hydrolysis methods aim to extract and purify MOS efficiently and in an environmentally friendly manner. These methods avoid the need for neutralizing the reaction medium or adding solvents that might alter the product's polymerization and purity. One approach involves using neutral or acidic detergents [38] . Another method employs ferrous chloride.[35] Subcritical water treatments also offer promising results.[39]Additionally, microwave and γ-ray radiation with water are used for hydrolyzing mannans in various plant seed gums.[40]

MOS purification is critical due to their potential as food additives and dietary prebiotics. Techniques like column chromatography, which uses gels, size exclusion chromatography, ion exchange, and activated carbon, allow for optimized separation conditions, enhancing oligomer separation and enabling cyclic operation and reuse.[41]Solvent purification, while straightforward, is limited by unsuitable solvents for consumable products. Solid additives can clean and remove salts from hydrolyzed solutions rich in MOS, showing promise in pilot-scale testing for scalability.[42] Membrane methods, effective for oligosaccharides separation and purification, require careful handling to prevent clogging and increased hydraulic resistance, especially for gelling products.[43]

MOS have diverse applications, primarily in animal feed and dietary supplements. MOS from mannan-rich plant waste biomass can promote the growth of beneficial probiotics such as *Bifidobacterium* and *Lactobacillus* species, enhancing gut health and inhibiting the adhesion of pathogenic bacteria.[38,44,45] MOS also exhibit anticancer activity, reducing the viability of human colon cancer cells, and possess antioxidant properties, demonstrating significant radical scavenging activity.[46,47] Additionally, MOS have shown potential in enhancing insulin resistance and glucose tolerance when combined with metformin, suggesting synergistic effects.[48]

4 CONCLUSION

Conventional methods for sugar extraction are frequently used to obtain MOS, but yields vary based on the mannan structure and the raw material components. Enzymatic hydrolysis, known for its specificity and environmental benefits, is the most studied method for extracting MOS from plant sources, though pretreatment is ideal to enhance enzyme access. Non-conventional methods, such as using organic acids for galactomannan hydrolysis, show promising yields. Further research is needed to optimize purification methods, considering their potential benefits for animal feed and dietary supplements. MOS from lignocellulosic biomass exhibit prebiotic properties with health benefits, including antioxidant activity, antibiotic replacement in feed, inflammation regulation, probiotic growth, and pathogen inhibition. This review provides valuable insights into the current state of MOS production and highlights key areas for future research. By evaluating technical conditions and selecting suitable alternatives for β-MOS production from vegetal sources, researchers and industry professionals can better harness the potential of MOS for various applications.

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