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Comparative study of alkali-soluble hemicelluloses isolated from bamboo (*Bambusa rigida*)

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ABSTRACT

The physicochemical properties and structural characteristics of seven alkali-soluble hemicellulosic preparations were determined. These were extracted from bamboo *(Bambusa rigida)* with 1 M NaOH, KOH, LiOH, $NH_3{\cdot}H_2O$, $(CH_3CH_2)_3N$, $Ca(OH)_2$, $Ba(OH)_2$, respectively, at 50 °C for 3 h, were comparatively studied. Sugar analysis showed that these hemicelluloses contained D-xylose as the major constituent, along with D-glucose and L-arabinose in noticeable amounts. Uronic acids, principally 4-*O*-methyl-D-glucuronic acid, occurred in a small amount. Furthermore, based on the sugar analysis and FTIR and NMR spectroscopy, it can be concluded that the hemicelluloses consist of a backbone of β-(1→4)-linked D-xylopyranosyl units having branches of arabinose and 4-*O*-methyl-D-glucuronic acid. Nitrobenzene oxidation revealed that the hemicelluloses obtained are mostly free of bound lignins. Moreover, it is noteworthy that hemicelluloses isolated with the different alkaline solutions presented different chemical compositions and slightly dissimilar structural features, indicating that alkalinity played an important role in cleaving the chemical linkages between the hemicelluloses and the lignins.

1. Introduction

The capture of solar energy through photosynthesis is a process that enables the storage of energy in the form of cell-wall polymers (that is, cellulose, hemicelluloses, and lignin). The energy stored in these polymers can be accessed in a variety of ways, ranging from simple burning to complex bioconversion processes.[1] Currently and most importantly, the research activities worldwide focus on biomass utilization, mainly in developing renewable byproducts, such as bioethanol, xylitol, and a great number of chemicals from forest and agriculture residues.[2]

Bamboo is the common term for a number of large woody grasses of a particular taxonomic group (subfamily *Bambusoideae*, family *Poaceae*) that are widely distributed in the Asian countries, such as China, and other Southeast Asian countries. To date, bamboo is mainly used in construction and reinforcing fibers, in paper, textiles, and construction boards, as well as in the food industry and bioenergy applications.[3] According to a research report by Scurlock et al.,[3] the cellulose content of bamboo is about 40–48% of the total mass. A cellulose content in this range makes bamboo a useful feedstock for paper production and for processes that convert cellulose to fuels, chemicals, and other biobased materials. Similarly, the lignin content of bamboo is 25–30%, compared to 11–27% reported for non-woody biomass, which more closely resembles the ranges reported for softwoods (24–37%) and hardwoods (17–30%). However, hemicelluloses (pentosans that usually amount to 22–35% in dry bamboo) should not be ignored because they can also be used in chemical conversions. Tomalang et al.[4] in their study also found that the main constituents of bamboo culms are holocellulose (60–70%), pentosans (20–25%), hemicelluloses and lignin (each of which amount to about 20–30%) and minor constituents like resins, tannins, waxes, and inorganic salts. Therefore, the large amounts of bamboo hemicelluloses are significant enough to be considered as a complementary source of raw material for different industries such as papermaking, baking, and food as well as non-food industries. Heretofore, there have been some studies that focused on the hemicelluloses of bamboos, yet the potential of this novel chemical has not completely been recognized due to its complex chemical structure.

Hemicelluloses, the second most abundant constituent of lignocellulosic biomass, are not chemically well-defined compounds but rather a family of polysaccharides composed of different five- and six-carbon monosaccharide units.[1] Generally, hemicelluloses found in higher plants contain a basic backbone of D-xylopyranosyl residues linked together by β-(1→4)-glycosidic bonds. Substituents

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such as arabinosyl, glucuronic acid, and acetyl groups, as well as various oligosaccharides, can be attached to the main chain at the two free OH groups of carbons C-2 and C-3 of the xylopyranose residue. In addition, phenolic acids such as ferulic acid and *p*-coumaric acid have been found to be etherified or esterified to O-5 of some arbinofuranose residues in arabinoxylans (AX).[5] Based on the hitherto reported review articles on the primary structure of xylans from various plant tissues, xylan-type polysaccharides can be divided into homoxylans and heteroxylans, which include glucuronoxylans, arabino (glucurono) xylans, glucurono (arabino) xylans, arabinoxylans, and complex heteroxylans.[6] In addition, the degree, type, and distribution pattern of the substitutions along the xylan backbone largely determine the structural properties. Because of their structural varieties and diversities, they can be utilized in their native and modified forms in various areas, including food and non-food applications.[7] It is for this reason that the industrial process for xylitol is by the hydrolysis of xylose-rich hemicelluloses to xylose, followed by hydrogenation of the xylose produced. Therefore, it appears especially important to study different plant hemicelluloses.

Based on studies in recent years, many methods have been developed to isolate hemicelluloses from the cell walls of agriculture residues. The hemicelluloses isolated from bamboo also have been investigated for decades.[8] Generally, hemicelluloses isolated with alkalis are commonplace, a fact that can be explained in that alkali isolation usually can be easily performed and it also has considerable cost advantage. However, the extractability of hemicelluloses varies with the alkali type and isolation conditions in different plants. In general, the alkaline treatment of lignocellulosic substances disrupts the cell wall by dissolving hemicelluloses and lignin, hydrolyzing uronic and acetic esters, swelling the cellulose and decreasing its crystallinity, and cleaving the α-ether linkages between lignin and hemicelluloses, as well as the ester bonds between lignin and/or hemicelluloses and hydroxycinnamic acids, such as *p*-coumaric and ferulic acids. The cleavage of *O*-acetyl groups cannot be avoided because the pH of the solution is at pH ~10, and all acetyl groups are hydrolyzed.[9,10] Although many literature reports address the different polysaccharides isolated with aqueous alkalis from various plants, little information about hemicelluloses of *Bambusa rigida* extracted with aqueous alkalis has been reported. Therefore, a comparative study of isolation and characterization of alkali-soluble hemicellulosic fractions of *Bambusa rigida* is of great importance in exploring and promoting the potential utilization of this biomass.

In the present study, the isolated bamboo hemicelluloses were studied by sugar analysis, alkaline nitrobenzene oxidation (NBO) of bound lignin, Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance spectroscopy (NMR), and gel-permeation chromatography (GPC), all of which provide significant evidence for the elucidation of the hemicellulosic structures of bamboo as well as the relationship between lignin and hemicelluloses.

2. Results and discussion

2.1. Yield and chemical composition

The hemicellulosic polymer is a mixture of a number of different polysaccharides, and the yield and composition of the polymer can vary depending on the method of isolation. Generally, the yield may be affected by the alkalis used in the experiment. Experimental data showed that the use of strong alkalis resulted in a higher yield of hemicelluloses when performed at given temperature (50 °C), suggesting that linkages between hemicelluloses and lignin were significantly disrupted and more of the hemicelluloses were dissolved. In the present study, the de-waxed bamboo powder was extracted at 50 °C for 3 h by various aqueous alkaline solutions, and the yields of the soluble hemicelluloses are shown in Table 1. The bamboo extracted with 1 M aqueous NaOH, KOH, LiOH, $NH_3{\cdot}H_2O$, $(CH_3CH_2)_3N$, $Ca(OH)_2$, and $Ba(OH)_2$ at 50 °C for 3 h yielded 6.4%, 6.0%, 7.2%, 5.0%, 6.1%, 4.2%, and 5.2% hemicelluloses (relative per cent of the de-waxed sample), respectively. However, it should be noted that H_5, extracted with $(CH_3CH_2)_3N$, presented a high yield of hemicelluloses (6.1% based on de-waxed matter), suggesting that triethylammonium chloride that was produced during the procedure of acidification may still remain in the hemicellulosic preparation. The high yields between H_1 and H_3 indicated that NaOH, LiOH, KOH under the conditions used significantly cleaved the ester bonds between the lignins and the hemicelluloses from the cell wall of bamboo by hydrolyzing the uronic and acetic acid esters, and by swelling the cellulose and decreasing its crystallinity, which resulted in a substantial dissolution of hemicellulosic polysaccharides and lignin macromolecules.[11] The yield of hemicelluloses can be also be explained by the accessibility of aqueous alkalis to the hemicellulosic surface.[12] In addition, different alkaline solutions have diverse disruption and dissolution abilities as they penetrate the cell wall. Additionally, the natural resistance of plant cell walls to chemicals eventually resulted in different yields of hemicelluloses. Generally speaking, strong alkali has the tendency to dissolve more hemicelluloses from a kibbled plant cell wall, although the crystalline cellulose core of a cell-wall can be decreased via decrystallization, such as by swelling bamboo with alkalis. By exposing more hemicelluloses under the dual treatment of disrupting and dissolution of alkalis, most of the hemicelluloses and lignin dissolve in the alkaline solution; however, there is still a portion of hemicelluloses and lignin that remains as an insoluble residue. This can be confirmed by the CP-MAS NMR spectrum of the residue after alkali extraction (spectrum not shown). This also indicates that a part of the ground substance (kibble) of the cell wall is still tightly linked together even after treatment with alkali, due to its limited penetration and dissolution of the cell wall.

The data on the sugar composition of hemicelluloses is given in Table 2. Obviously, xylose was a predominant sugar constituent in the seven hemicellulosic preparations, comprising 63.26–81.82% of the total sugar composition, whereas glucose (7.34–25.29%) and arabinose (5.43–6.90%) were present in small amounts. Galactose

Table 1
Yield of hemicelluloses solubilized during treatments of de-waxed bamboo with various alkalis at 50 °C for 3 h

Fraction	Yield (% dry matter)
H_1, obtained by extraction with 1 M NaOH	6.4
H_2, obtained by extraction with 1 M KOH	6.0
H_3, obtained by extraction with 1 M LiOH	7.2
H_4, obtained by extraction with 1 M $NH_3{\cdot}H_2O$	5.0
H_5, obtained by extraction with 1 M $(CH_3CH_2)_3N$	6.1
H_6, obtained by extraction with 1 M $Ca(OH)_2$	4.2
H_7, obtained by extraction with 1 M $Ba(OH)_2$	5.2

Table 2
The relative content of sugars and uronic acids in the isolated hemicelluloses

Sugars	Hemicellulosic fractions[a]						
	H_1	H_2	H_3	H_4	H_5	H_6	H_7
Arabinose	6.90	5.43	6.11	5.57	5.37	6.18	5.68
Galactose	1.15	0.86	0.76	2.79	3.12	1.73	0.93
Glucose	7.56	7.34	10.09	23.06	25.29	19.06	9.85
Xylose	78.39	81.82	77.41	65.38	63.26	69.32	78.81
Uronic acid	6.00	4.54	5.63	3.19	2.96	3.71	4.73

[a] Corresponding to the hemicellulosic fractions in Table 1.