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Note

Preliminary investigation of the association of inorganic cations with carboxylic acid groups in wood

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Recent studies in this laboratory concerning the application of catalysts for the combustion and gasification of wood have suggested that the naturally occurring, inorganic species in wood are exchangeable with ions added from solution[1], and that soaking wood in an inorganic salt solution, followed by thorough washing with distilled water, affords a highly reproducible level of addition[2]. These findings indicate the potential role of ion-exchange sites in wood in binding cations of inorganic salts and in controlling the proportion of inorganic species retained in the wood. Cell-wall ion-exchange processes have been studied with respect to nutrient transport in developing plant-tissues[3], but very little information is available on the ultimate state of ion-exchange sites in the mature wood cell walls.

The most probable ion-exchange sites in such hardwoods as cottonwood are 4-*O*-methyl-D-glucuronic acid substituents in the xylan, and unesterified D-galacturonic acid groups in the pectins. In this study, the extent of ion exchange in the uronic acids of the cell wall has been examined by analyzing samples of untreated, acid-washed, and potassium-exchanged cottonwood by Fourier-transform infrared spectroscopy (F.t.i.r.), in order to ascertain the relative abundance of the carboxylic acids and carboxylate anions according to the absorptions at 1730 and 1600 cm^{-1}, respectively.

EXPERIMENTAL

Cottonwood sapwood *(Populus trichocarpa)* was ground in a Wiley mill and the 20 × 35 Tyler-mesh fraction was retained. The sample was analyzed for Klason lignin content by standard methods[4]. Ash content was determined by thermogravimetry (TG) using a Perkin–Elmer TGS-2 system. The carboxyl content of the wood was determined by absorption of Methylene Blue[5]. All samples were dried at 60° under diminished pressure.

Acid-washed cottonwood was prepared by stirring the ground wood in 0.1M HCl for 4 h at room temperature. The suspension was filtered, and the wood was

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thoroughly washed with distilled water, and dried. The ion-exchanged sample was prepared by suspending the acid-washed wood (1 g) in 0.01M K_2CO_3 solution (100 mL) for 30 min, followed by filtering, washing thoroughly with distilled water, and drying. An alkali-hemicellulose sample was isolated by direct extraction of the ground wood with 16% KOH, using a modification of the method described by Adams[6]. Repeated attempts to isolate hemicellulose by extraction with Me_2SO gave very low yields, and this approach was not pursued further.

Internal-reflectance infrared spectra of whole-wood samples were recorded with a Nicolet 10MX F.t.i.r. spectrometer, using a Harrick reflectance accessory with a KRS-5 reflection element (45°; 50 × 10 × 3 mm). The background spectrum was taken through a clean KRS-5 reflectance element. Samples for reflectance spectroscopy were prepared by powdering the wood sample in a vibratory ball mill for 5 min, suspending the powdered wood in D_2O for 10 min, and then filtering the suspension, with suction, through glass filter paper on a Büchner funnel. The filter paper was then washed with D_2O, dried with suction for ~15 min, and cut into pieces in the shape of the reflectance element. This treatment was intended to replace adsorbed water with D_2O, rather than to effect deuterium exchange of hydroxyl or acid groups. By using this method, the wood retained enough plasticity to provide good contact with the reflectance element, and there was little interference from the H_2O absorption band at 1640 cm^{-1}. Infrared spectra of isolated hemicellulose samples were recorded for films prepared by evaporation of aqueous hemicellulose solutions.

Analysis of the component monosaccharides in the hemicelluloses was carried out at the University of Colorado Department of Chemistry by gas–liquid chromatography of trimethylsilyl ethers of the methyl glycosides of the sugars in the hydrolyzates[7].

RESULTS AND DISCUSSION

Chemical analyses of the cottonwood sample and of an isolated alkali-hemicellulose fraction are shown in Table I. Additional analytical data on a different sample of this species have previously been published[8]. The results in Table I

TABLE I

CHEMICAL ANALYSIS OF COTTONWOOD SAPWOOD AND OF AN ISOLATED ALKALI-HEMICELLULOSE FRACTION (DRY, ASH-FREE BASIS)

Sample	*Polysaccharide (%)*	*Klason lignin (%)*	*Ash (%)*	*Elemental analysis*		
				C	*H*	*O*[a]
Cottonwood	76.3	20.5	0.41 ±0.01	48.6	6.3	45.1
Hemicellulose (alkali)	(100)	—	4.70 ±0.40	45.6	6.4	48.0

[a]Oxygen by difference.

are in good agreement with the analyses expected for a typical hardwood species.

The alkali-hemicellulose fraction was originally isolated in good yield, but was contaminated with a large proportion of potassium acetate. On repeated washing with 95% ethanol (to remove the potassium acetate), much of the polysaccharide was lost, and the final yield was only 4% of the weight of the original wood. Analysis of the component monosaccharides of the alkali-hemicellulose fraction showed it to be composed of 92.2% of xylose, 7.2% of 4-*O*-methylglucuronic acid, and <1% of arabinose and rhamnose. Thus, the hemicellulose is almost pure 4-*O*-methylglucuronoxylan, and the 4-*O*-methylglucuronic acid substituents number one per every 18 xylosyl residues. This level of substitution is about half the value previously reported for this specimen on the basis of methoxyl analysis of an isolated xylan sample[8].

Analysis of the carboxyl content of untreated and acid-washed wood samples by the Methylene Blue-absorption method gave values of 8.1 and 8.7 meq/100 g, respectively. Because the Methylene Blue method is insensitive to the state of the carboxyl group[4], the higher value for the acid-washed wood is possibly due to partial hydrolysis of ester groups. Based on a glucuronoxylan content[8] of 21% and a polymer repeating unit consisting of 18 xylosyl residues, 9 acetyl substituents, and one 4-*O*-methylglucuronic acid substituent (calculated on the basis of the monosaccharide analysis just reported and the acetyl content given in ref. 8), a 4-*O*-methylglucuronic acid content of 6.3 meq/100 g may be calculated for whole cottonwood. This value compares well with that obtained by Methylene Blue absorption, and suggests that (*1*) the alkali-hemicellulose fraction is representative of the 4-*O*-methylglucuronoxylan in this species and (*2*) the 4-*O*-methylglucuronic acid groups in the hemicelluloses constitute the primary source of carboxyl groups.

Transmission-F.t.i.r. spectra of films prepared from aqueous solutions of (A) an untreated, and (B) a dilute acid-treated, alkali-hemicellulose sample are shown

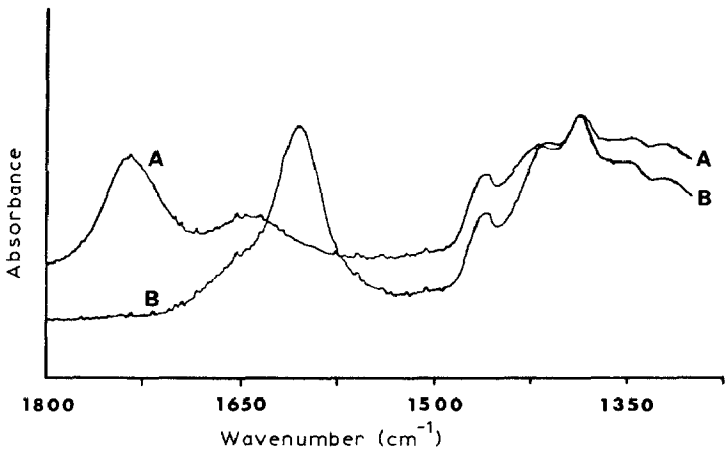

Fig. 1. F.t.i.r. spectra of films prepared from an isolated alkali-hemicellulose fraction. Trace (A), as isolated in potassium salt form; (B), after treatment with dilute acid.

in Fig. 1. These spectra show the shift in the carbonyl stretching frequency of the acid groups from 1604 cm^{-1} for the untreated hemicellulose (isolated as the potassium salt) to 1734 cm^{-1} for the acid-treated sample. The frequencies of the absorptions are ~5 cm^{-1} higher than those given in the literature for these functional groups[9,10]. The absorption near 1650 cm^{-1} is due to adsorbed water. The absence of absorbance at 1730 cm^{-1} in the spectrum of the untreated hemicellulose sample confirmed that all of the acetate substituents had been hydrolyzed during the alkaline extraction.

Fig. 2 shows the reflectance-F.t.i.r. spectra of untreated, ion-exchanged, and acid-washed ground cottonwood samples in the 1800 to 1300-cm^{-1} range. As mentioned previously, these samples were treated with D_2O prior to analysis, in order to minimize the absorbance due to adsorbed water. Interpretation of these spectra in terms of the state of the carboxylic acid groups is not straightforward, because of the interfering absorbances of lignin at 1595 cm^{-1} and of acetyl groups of the hemicelluloses[10] at 1730 cm^{-1}. The contribution of the carboxylic acid groups to each of the peaks was expected to be small. The acetyl groups are almost ten times as plentiful as the acid groups on the basis of the analysis already reported. Similarly, the contribution of the carboxylate anion to the peak at 1600-1595 cm^{-1} is small compared to the absorbance due to the more prevalent, and strongly absorbing, benzene rings in lignin.

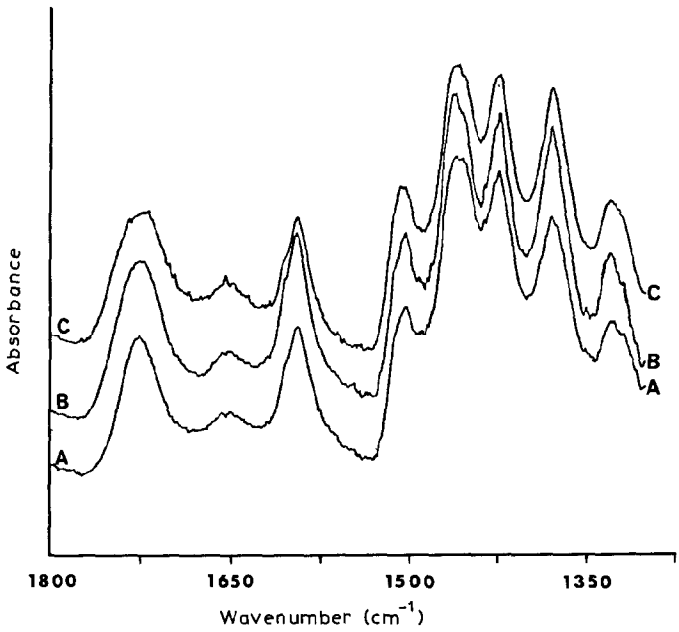

Fig. 2. Reflectance-F.t.i.r. spectra of deuterated samples of (A) acid-washed, (B) untreated, and (C) K^+-exchanged ground cottonwood.

Despite these complications, comparison of untreated wood with samples of acid-washed wood, in which all of the carboxyl groups are in the acid form, and with ion-exchanged wood, in which all of the carboxyl groups are in the carboxylate anion form, does allow some conclusions to be drawn relative to the state of the carboxylic acid groups in untreated wood.

The spectra shown in Fig. 2 do not reveal any qualitative differences therein due to the different sample treatments. However, as shown in Table II, quantitative analysis by integration of the absorbances due to the combined (acetyl/CO_2H) and (lignin/COO^-) groups indicates subtle differences between the absorbances in the spectra of each of the samples. The absorbances were integrated over the spectral range indicated in Table II, using the quantitation software of the Nicolet 10MX F.t.i.r. instrument, which measures the area above a tangential baseline between the values of the absorption curve at the limits of the spectral range of interest. Because of the potential effect on the baseline of the absorbance due to the adsorbed water remaining, each peak was also quantified by "trapezoidal" integration over the same spectral ranges, above a baseline between the minima at either end of the spectral range containing both the acid and carboxylate anion absorptions (1771–1543 cm^{-1}). In this case, the spectra were plotted on an expanded scale, and the peaks of interest were carefully excised and weighed.

The results of quantitation by either method show a shift in absorption from the (lignin/COO^-) peak to the (acetyl/CO_2H) peak when the untreated wood is washed with acid, and this shift is reversed when the acid-washed wood is treated with a solution containing potassium ions. Both methods of integration show that

TABLE II

QUANTITATIVE ANALYSIS OF REFLECTANCE-F T I R ABSORBANCES DUE TO CARBOXYLIC ACID AND CARBOXYLATE ANIONS IN COTTONWOOD SAMPLES[a]

Method of integration	*Sample treatment*	*Integrated absorbance (arbitrary units)*	
		Acetyl/CO_2H (1771–1678 cm^{-1})	*Lignin/COO^- (1628–1543 cm^{-1})*
Tangential baseline	untreated	3.30 (60%)	2.16 (40%)
	acid-washed	2.77 (66%)	1.45 (34%)
	K^+-exchanged	2.40 (57%)	1.80 (43%)
Trapezoidal baseline	untreated	148 (58%)	107 (42%)
	acid-washed	134 (63%)	80 (37%)
	K^+-exchanged	121 (56%)	97 (44%)

[a]Absorbances were quantified by integration over the wavenumber range indicated.

the distribution of the absorbances in untreated wood is intermediate between that of the acid-washed and ion-exchanged samples, but more similar to that of the ion-exchanged sample. This provides evidence that the carboxylic acid groups in mature wood exist to some extent, and possibly to a large extent, as carboxylate anions, presumably in association with metal cations that comprise the inorganic fraction.

In this context, it is instructive to compare the carboxyl content of wood with the proportion of inorganic materials (ash). Table I shows that the cottonwood used in this study contained 0.41% of ash. The ash had previously been analyzed, and found[1] to contain Ca, 870 p.p.m.; K, 670 p.p.m.; and Mg, 320 p.p.m. This study has shown that the cottonwood contains ~8 meq of carboxyl groups per 100 g of wood, primarily in 4-*O*-methylglucuronic acid substituents of the xylan. These acid groups would have the capacity of complexing approximately 1500 p.p.m. of Ca, 2900 p.p.m. of K, or 900 p.p.m. of Mg. Thus, the D-glucuronic acids have sufficient ion-exchange capacity to complex a large percentage of the inorganic constituents in wood, and the data presented suggest that at least part of the inorganic fraction in cottonwood is complexed in this way.

The results of this study do not agree with those reported by Timell[11], who cited a differential infrared-spectroscopy study in which he found that the 4-*O*-methylglucuronic acid groups are not present as carboxylate anions. Other authors have asserted that all of the D-glucuronic acid groups in another plant fiber are involved in ester linkages to lignin, and that the ion-exchange capacity of the fiber is due to free phenolic groups in the lignin[12]. Although there is strong evidence for ester linkages involving D-glucuronic acid groups, the data presented here indicate that carboxylate anions are also present in untreated cottonwood; it would, therefore, be interesting to study additional species, in order to determine whether these trends can be demonstrated in a broader sample.

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