0273-2289/90/2425—0041$02.00

Pyrolytic Conversion of Biomass to Anhydrosugars

Influences of Indigenous Ions and Polysaccharide Structures

Scientific Note

GLENN R. PONDER, HANG-XIA QIU,
AND GEOFFREY N. RICHARDS*

*Wood Chemistry Laboratory, University of Montana,
Missoula, MT 59812*

Index Entries: Pyrolysis; biomass; wood; polysaccharides; anhydrosugars.

INTRODUCTION

The production of high yields of 1,6-anhydroglucose [1] (predominantly pyranose, with some furanose) from pyrolysis of cellulose is well known. Yields of up to 66% from pure cellulose are produced by vacuum pyrolysis when all metal ions or salts are removed before pyrolysis (*1*). The production of [1] from wood in high yield also requires the prior removal by acid washing of the indigenous metal ions that are bound by ion exchange to the hemicelluloses in the wood (2). Thus, the yield of [1] from pyrolysis of acid washed cottonwood was 9% based on total wood, or 20% based on cellulose (3). The mechanism of formation of [1] in pyrolysis of cellulose has been the subject of frequent speculation in the past (*4*), and we have recently posited a new hypothesis (*1*), which we are currently testing. We have also shown recently (5) that pendant L-arabinofuranoside units in several plant cell wall (biomass) materials are converted by pyrolysis to 1,5-anhydro-L-arabinofuranose [2] and that the efficiency

---

*Author to whom all correspondence and reprint requests should be addressed.

of this pyrolytic conversion is considerably increased, up to 78% conversion, by prior removal of indigenous metal ions by acid washing.

EXPERIMENTAL

Materials

The sapwood of a 20-yr-old black cottonwood (*Populus trichocarpa*), felled several years previously and stored under ambient conditions, was Wiley-milled to −80 mesh. The sapwood of a 35-yr-old ponderosa pine (*Pinus ponderosa*), felled 2 yrs previously, was treated in the same way. Both samples were acid washed by immersion of a 10 g sample in 0.05 *M* hydrochloric acid, degassing under vacuum, and then washing in a column with 1 L of the same acid (12 h), followed by deionized water of resistivity greater than 18 megohm/cm. Metal ion contents of the woods were determined by inductively coupled plasma spectrometry.

Glycose analyses were carried out by hydrolysis, initially with 72% sulfuric acid, followed by reduction to alditols, acetylation, and gas chromatography, as described earlier (*8*), using myoinositol added to the sample as internal standard before hydrolysis and correcting for acid degradation of glycoses. Uronic acids were determined on the same hydrolysates, using the 3-hydroxydiphenyl reagent (*8*).

Pyrolysis and Analysis of Products

Vacuum pyrolyses were carried out in aluminum boats in a tube furnace carrying a flow of nitrogen at 1–2 mm Hg at 350°C for 30 min or at 500°C for 5 min, as described earlier (*9*). The volatiles that condensed in a glass tube at room temperature immediately after leaving the heated zone are designated as "tars," and the anhydro sugars were found only in this fraction. Samples of tar (10 mg) plus glucitol (1 mg) as internal standard were trimethyl silylated with BSTFA containing 1% TMCS (Pierce Chemical Co., IL) in dry pyridine and analyzed by gas chromatography (*10*) on a 3% SE52 packed column at 130°+6°/min. The derivatives of the four anhydro sugars had retention times of 0.72 [1], 0.38 [2], 0.67 for 1,6-anhydro-β-D-galactopyranose [3], and 0.70 for 1,6-anhydro-β-D-mannopyranose [4] relative to glucitol, 1.00. The other major products in the gas chromatogram were 1,2,3-trihydroxybenzene (0.52) and 1,2,4-trihydroxybenzene (0.59). Yields were calculated from peak areas relative to glucitol using response factors determined with authentic compounds (*10*).

RESULTS AND DISCUSSION

As part of a systematic study of mechanisms of pyrolysis of polysaccharides and lignocellulosics, we now report on the relative efficiencies of

Table 1
Metal Ion Contents[a]

Sample	Ca	Mg	Mn	P	K	Na	Zn
Cottonwood	1500	200	ND	140	1000	30	9
Acid-washed Cottonwood	12	1	0	8	5	7	0
Ponderosa Pine	678	316	107	64	779	10	11
Acid-washed Ponderosa Pine	0	1	1	15	12	11	0

[a] PPM based on wood.

Table 2
Content of Glycan in Acid-Washed Wood[a]

	Glycan content, % of dry matter					
	Arabinose	Xylose	Mannose	Galactose	Glucose	Uronic Acid
Cottonwood	0.2	14.9	2.65	0.7	41.8	4.9
Ponderosa Pine	1.05	8.3	10.0	2.25	39.7	4.45

[a] Averaged duplicate analyses on each wood, calculated as anhydroglycan.

conversion of the major polysaccharide components of wood into simple anhydrosugars. We have studied a softwood (ponderosa pine, *Pinus ponderosa*) and a hardwood (cottonwood, *Populus trichocarpa*), using the sapwood in each case and removing indigenous metal ions by acid washing at ambient temperature. The major metal ions before and after acid washing are shown in Table 1 and the absolute glycan contents in Table 2. We conclude that both woods contain predominantly cellulose and that pine (like most softwoods) (*6,7*) contains a major component of a mannan, presumably a galactoglucomannan, which is "the predominant hemicellulose in the wood of all gymnosperms" (*7*). The xylans are assumed to be present as arabino-(4-0-methylglucurono)xylans in the pine and as *O*-acetyl-(4-0-methylglucurono)xylans in the cottonwood, as is typical for gymnosperms and angiosperms, respectively (*7*).

The major volatile products and their yields from vacuum pyrolysis of the acid washed woods are shown in Table 3. The 1,6-anhydroglucopyranose [1] was accompanied, as is usual for pyrolysis of glucans, by a small amount of the furanose isomer (pyranose:furanose; 1:0.08 at 350°C and 1:0.03 at 500°C). The mechanism of formation of the furanose isomer is not known, and it is not included in yields of [1]. It is possible that furanose isomers of [3] and [4] are also present in small amounts and not detected in this analysis. The efficiency of conversion of a total hexose in the wood into the corresponding anhydrosugar is shown in Table 4.

Table 3
Products from Vacuum Pyrolysis of Acid-Washed Wood[a]

	Cottonwood		Ponderosa Pine	
Pyrolysis Temperature, C	350°	500°	350°	500°
1,6-anhydro-β-D-glucopyranose [1]	5.7	8.1	8.1	10.1
1,5-anhydro-β-L-arabinofuranose [2]	ND	ND	ND	
1,6-anhydro-β-D-galactopyranose [3]	0.2	0.25	0.6	0.7
1,6-anhydro-β-D-mannopyranose [4]	0.35	0.45	1.8	2.3
1,2,3-trihydroxybenzene	ND	0.4	0.4	0.6
1,2,4-trihydroxybenzene	ND	0.7	0.8	0.9

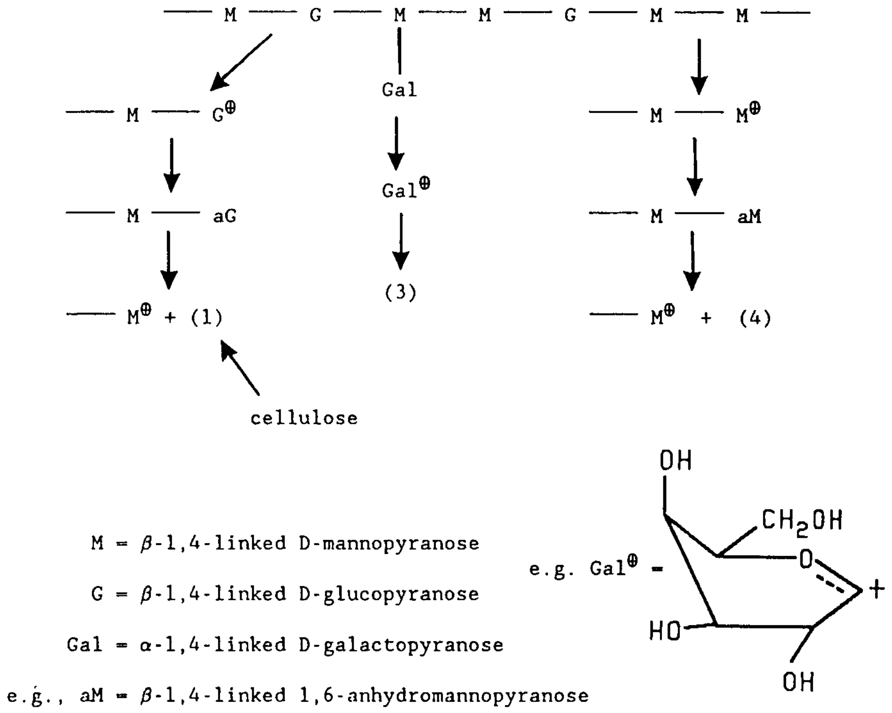
[a] Yield percent based on wood.

Table 4
Pyrolytic Conversion of Wood Glycans to Anhydrosugars (%)[a]

	Cottonwood		Ponderosa Pine	
Pyrolysis Temperature, C	350°	500°	350°	500°
1,6-anhydroglucopyranose [1]	14	19	21	25
1,6-anhydrogalactopyranose [3]	29	36	27	31
1,6-anhydromannopyranose [4]	13	17	18	23

[a] Based on total glycose content in wood sample (Table 2).

The predominant modes of pyrolysis to be expected in a galactoglucomannan are shown in Scheme 1. This type of hemicellulose is most abundant in gymnosperms and does not vary significantly in structure between genera or species (*7*). The general pyrolysis reactions shown are in accordance with our recent hypotheses for the mechanism of formation of levoglucosan [1] from cellulose (*1*). The first steps shown are analogous to hydrolysis of glycosidic bonds and generate cations, such as the galactopyranosyl unit shown in Scheme 1. In the case of this latter hexose (because it is entirely present as nonreducing end groups (*7*)), the volatile 1,6-anhydride [3] forms directly by nucleophilic addition of the C_6 oxygen to C_1; it then enters the vapor phase and is condensed as liquid "tar." Hence, conversion of galactose in the wood into [3] is relatively efficient. In the case of mannose and glucose (the latter being present both in the hemicellulose and cellulose), the scission of a mannosyl or glucosyl bond produces first a glycosyl cation, and then a 1,6-anhydroglycose unit at the end of a shortened polysaccharide chain (Scheme 1). This product is not volatile, and hence remains in the solid phase, but any subsequent scission of its penultimate glycosyl bond yields the volatile [1] or [4]. The additional steps involved in formation of [1] and [4] compared with [3], with the resultant increased opportunity for competing reaction pathways, are the most likely cause of the lower efficiency of pyrolytic conver-

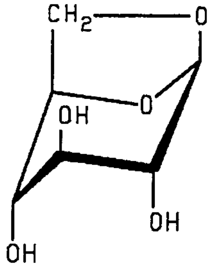


Scheme 1. Pyrolysis of Galactoglucomannan.

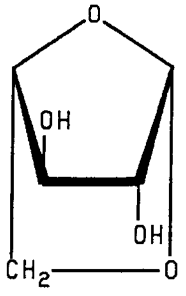
sion of glucose and mannose in the wood into [1] and [4], respectively (*see* Fig. 1). It is recognized that the acid hydrolysis of galactopyranosides occurs rather more rapidly than the corresponding mannose and glucose isomers (*13*) and that this effect may be reflected in analogous relative rates of pyrolytic scission in the galactoglucomannan, thus also contributing to the more efficient pyrolytic conversion of galactose to [3]. The pyrolytic situation, however, is more complex than acid hydrolysis since it is also necessary to consider the conformational factors involved in conversion of the initial glycosyl cations into the 1,6-anhydrides.

There is little doubt that the pendant arabinofuranoside units in the woods are converted relatively efficiently by pyrolysis into 1,5-anhydroarabinofuranose [2]. However, the pyrolysis of the polysaccharides also produces small amounts of 1,4-dihydroxybenzene and 5-(hydroxymethyl)-furfural, which elute almost coincidentally with [2] in the gas chromatographic analysis (*10*). Consequently, in these woods with low arabinose content, we are unable to determine accurately the pyrolytic conversion efficiency for arabinose.

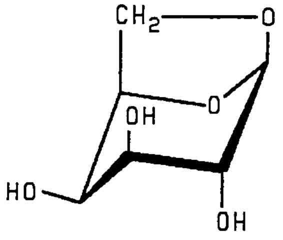
There remains the question of the pyrolytic fate of xylose units, which are a major component of wood in the xylan hemicelluloses, and of the 4-0-methylglucuronic acid units, which are bonded to them. We have already shown that the decarboxylation of uronic acids is one of the earliest events in the pyrolysis of wood (*11*), and it is probable that the remainder of a de-



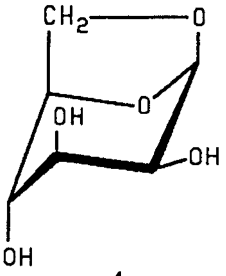
1



2



3



4

1=1,6-ANHYDRO-β-D-GLUCOPYRANOSE
2=1,5-ANHYDRO-β-L-ARABINOFURANOSE
3=1,6-ANHYDRO-β-D-GALACTOPYRANOSE
4=1,6-ANHYDRO-β-D-MANNOPYRANOSE

carboxylated uronic acid degrades relatively unspecifically to low molecular weight fragments. The 1,4-xylan chain should be subject to the same type of pyrolytic scission as shown in Fig. 1, but in the resultant xylopyranosyl cation, there is no hydroxymethyl group available for nucleophilic attack on C_1. It is conceded that, under pryolytic conditions, the C_4 oxygen could add to C_1 in an isolated xylopyranosyl cation, but the cation produced by scission of the xylan has the C_4 oxygen substituted, and, hence, nucleophilic attack on C_1 by this oxygen is very unlikely. Thus, we conclude that the xylopyranosyl cation from xylan cannot be stabilized by conversion to an anhydride and is subject to less specific degradation to complex low molecular weight products.

The 1,2,3- and 1,2,4-trihydroxybenzenes have been reported previously from pyrolysis of cellulose (*12*) and are believed to be pyrolysis products of polysaccharides. Their formation was previously assumed to be favored by the presence of salts, but this present work shows that they are also formed in the absence of salts. Probably, they are more readily detected in pyrolyses carried out in the presence of salts because the salts suppress the formation of the anhydro sugars, which are alternative products of the pyrolysis.

ACKNOWLEDGMENT

This work was financially supported by the McIntire Stennis Project MNOZ8701.

REFERENCES

1. Essig, M., Richards, G. N., and Schenk, E. *Appl. Pol. Symp.*, in press.
2. DeGroot, W. F. (1985), *Carbohydr. Res.* **142,** 172–178.
3. Shafizadeh, F., Furneaux, R. H., Cochran, T. G., Scholl, J. P., and Sakai, Y. (1979), *J. Appl. Pol. Sci.* **23,** 3525-3539.
4. Antal, M. J. (1983), *Adv. in Solar Energy* **61,** 61–111.
5. Essig, M. and Richards, G. N. (1988), *Carbohydr. Res.* **181,** 189–196.
6. Pettersen, R. C. (1984), *The Chemistry of Solid Wood,* Rowel, R., ed., ACS Adv. in Chem. Series, Washington, DC, pp. 115, 116.
7. Timell, T. E. (1965), *Adv. in Carbohydr. Chem.* **20,** 410–483.
8. Neilson, M. J. and Richards, G. N. (1982), *Carbohydr. Res.* **104,** 121–138.
9. Bradbury, A. G. W., Sakai, Y., and Shafizadeh, F. (1979), *J. Appl. Pol. Sci.* **23,** 3271-3280.
10. Lowary, T. L. and Richards, G. N. (1988), *J. Wood Chem. and Tech.* **8,** 393–412.
11. DeGroot, W. F., Pan, W.-P., Rahman, M. D., and Richards, G. N. (1988), *J. Anal. and Appl. Pyrol.* **13,** 221-231.
12. Richards, G. N., Shafizadeh, F., and Stevenson, T. T. (1983), *Carbohydr. Res.* **117,** 322-327.
13. BeMiller, J. N. (1967), *Adv. Carbohydr. Chem.* **22,** 25–108.