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1,5-ANHYDRO-β-L-ARABINOFURANOSE FROM PYROLYSIS OF PLANT CELL WALL MATERIALS (BIOMASS)

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ABSTRACT

Three types of agricultural waste material having a significant content of L-arabinose have been subjected to mild, vacuum pyrolysis, and yields of 1,5-anhydro-L-arabinofuranose (**1**) determined. In corn bran, ~ 40% of the L-arabinose is converted into **1**, and this conversion is increased to 78% when the bran is subjected to prior acid washing. The inner and outer barks of ponderosa pine give ~ 30% conversion of their L-arabinose content into **1**, but orange peel gives only 9% conversion. A mechanism is postulated involving pyrolytic scission of pendant L-arabinofuranose units from polysaccharides, with cyclization to produce **1**.

INTRODUCTION

The pyrolysis of plant cell-wall material, often referred to as biomass, has been extensively studied[1]. The major motivation in such work is usually the desire to obtain a product of higher value from such low-value materials as agricultural wastes[2]. The major component of such materials is usually cellulose, and this is converted by pyrolysis into levoglucosan (up to 60% yield from purified cellulose[3]) or levoglucosenone (~ 10% yield from pure cellulose with acid catalysis[4]). The other major components of plant cell-wall materials are hemicelluloses and lignin. These begin to pyrolyze at lower temperatures than does cellulose[5]. Little is known of the reactions involved in lignin pyrolysis, but we have shown that the first events in the pyrolysis of hemicelluloses are the loss of L-arabinose, decarboxylation and subsequent decomposition of alduronic acids, and release of acetyl groups as acetic acid[5]. We now describe an investigation of the fate of the L-arabinose in such systems.

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TABLE I

CONTENT OF NEUTRAL GLYCAN IN BIOMASS

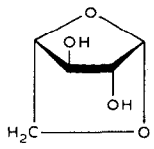
Biomass material	*Glycan content (% of dry matter)*					
	Rhamnose	*Arabinose*	*Xylose*	*Mannose*	*Galactose*	*Glucose*
Corn bran (original)		3.7	4.6		3.0	6.9
Corn bran (activated)		13.6	23.7	tr.[a]	2.3	14.7
Acid-washed corn bran		13.8	24.5	tr.	2.4	15.3
Ponderosa pine, outer bark		3.5	0.9	1.7	1.1	14.6
Ponderosa pine, inner bark		5.1	1.1	0.9	1.2	25.6
Orange peel	1.9	4.2	1.2	1.1	3.1	21.0

[a]tr. = trace.

RESULTS AND DISCUSSION

A range of agricultural waste materials was selected on the basis of L-arabinose content and is listed in Table I. The analyses in Table I were carried out by hydrolysis with 72% sulfuric acid followed by reduction, acetylation, and gas-liquid chromatography (g.l.c.), using *myo*-inositol as internal standard added before hydrolysis, and corrected for acid degradation of glycoses[6]. Uronic acids were present, especially in orange peel, but were not quantitatively determined. The corn bran gave very low and inaccurate results when analyzed as received, because of incomplete hydrolysis. This effect may be due to[7] "hornification" by drying or by other heating of the bran causing resistance to hydrolysis. The bran was activated by soaking in water overnight at room temperature, and then freeze-drying and we consider that the glycan contents given for the activated bran are accurate. The acid washing of the bran, to remove metal ions and salts, was carried out under mild conditions (0.02M hydrochoric acid at room temperature) to minimise hydrolysis of L-arabinofuranose units. The values in Table I show a slight increase in all glycan contents after acid washing, due to the diminution in the ash content.

The corn bran represents a wide range of debris from milling of maize, and has been treated to remove much of the starch originally present. The structures of the polysaccharides in corn bran have not been extensively studied, but wheat bran has been shown to consist of cell-wall material from the pericarp, seed coat, aleurone layer, and endosperm. Its preponderant hemicellulose is a highly branched arabinoxylan (A:X = 1.00:1.14), and the L-arabinose is present mainly as pendant arabinofuranose units[8]. This material is probably similar to the hemicellulose of the corn bran used in this study. The D-glucan content probably represents partly cellulose and partly ((1→3))-(1→4)-linear D-glucan from the same cell-wall source[9]. The inner and outer barks contain cellulose, hemicelluloses, and pectate polysaccharide



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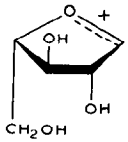

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components, with higher proportions of all types of polysaccharide in the phloem. In these samples, the L-arabinose is present as single L-arabinofuranose units in hemicellulose, and as more-complex L-arabinan structures in the pectic substances[9]. It is probable that, in the orange peel, the L-arabinose occurs mainly in pectic substances[9].

The procedure selected was the batch vacuum-pyrolysis of the biomass for a limited period at the lowest temperature at which formation of condensible volatile compounds (tars) could be observed. The objective was to minimize formation of levoglucosan and other products which are formed at higher temperatures from cellulose. The tars were analyzed by g.l.c. after formation of trimethylsilyl (Me_3Si) ethers. In the case of corn bran, only one major g.l.c. peak was observed: it was subsequently shown to be that of 1,5-anhydro-β-L-arabinofuranose (**1**). A sample of tar from corn bran pyrolyzed at 300° was chromatographed on silica gel to yield pure **1** and this was used to determine response factors *versus* D-glucitol for Me_3Si g.l.c. analysis of the content of **1** in each of the tar products. The results are shown in Table II.

In an attempt to limit to pyrolysis reactions to the conversion of arabinose into **1** and, hence, to obtain the maximum concentration of **1** in the tar, attempts were made to determine minimum pyrolysis conditions. The sequence of pyrolysis of corn bran at 300° for times decreasing from 60 to 20 min showed little effect of time on the yield of tar, the concentration of **1** in the tar, or the efficiency of conversion of L-arabinose into **1**. It is probable that most of the conversion of L-arabinose into **1** occurs in less than 20 min at 300°. By lowering the pyrolysis temperature to 280° and 260° for 30 min, the total conversion of arabinose into **1** was lessened, as was the total yield to **1** from biomass, but the concentration of **1** in the tar was significantly raised (from 24 to 31 percent). A much greater effect was, however, produced by acid-washing of the bran, which raised to 78% the pyrolytic conversion of L-arabinose into **1**, with the content of **1** in the tar being 49%. This effect is reminiscent of

TABLE II

YIELDS OF ANHYDRO-L-ARABINOSE (1) AND PYROLYSIS CONDITIONS

Biomass material	*Conditions of pyrolysis*		*Yields (% dry matter)*		*Yield of* **1** *(% of biomass)*	*Content of* **1** *in tar (%)*	*Conversion (%) of* L-*arabinose into* **1**
	Time(min)	*Temp (°C)*	*Tar*	*Char*			
Corn bran	60	300	26	n.d.[a]	6.0	24	44
	30	300	27	n.d.	6.5	24	47
	20	300	20	n.d.	5.3	27	39
	30	280	17	68	4.9	29	36
	30	260	13	81	4.0	31	29
Acid-washed corn bran	30	300	22	60	10.65	49	78
Pine, outer bark	30	300	18	61	1.3	7	37
Pine, inner bark	30	300	18	40	1.35	8	26
Orange peel	30	300	12	53	0.4	3	9

[a]n.d. = not determided.

TABLE III

^{1}H-N.M.R. VALUES[a] for **1**

Solvent	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*$_{exo}$	*H-5*$_{endo}$	*OH-2*	*OH-3*
Acetone-d_6	5.33(brs)	3.75(s)	3.53–3.60(o)[b]	4.52(d)	3.43(dd)	3.56(dm)	3.75(o)[b]	4.32(d)
Acetone-d_6 + D_2O	5.34(d)	3.77(brs)	3.38–3.62(o)[b]	4.55(brd)		3.38–3.62(o)[b]		

[a]Me_4Si as internal standard. [b] o = obscured.

the dramatic increase in the yields of 1,6-anhydro-D-glucose from the pyrolysis of cellulose when the latter is first washed with acid[3]. The increase in anhydro sugar formation from pyrolysis of the polysaccharides appears to be associated especially with removal of metal ions, which probably catalyze alternative mechanisms for degradation of such intermediates[10] as **2**.

The pyrolysis of both inner and outer bark resulted in rather lower efficiency in the conversion of L-arabinose into **1** than was observed for corn bran and, because of the lower L-arabinose content of the barks, a much lower overall yield. Both the inner and outer barks have high ash contents, however, and it is probable that much higher conversion into **1** would be achieved after acid washing of the barks. The conversion of L-arabinose in orange peel into **1** was found extremely inefficient, and it appears that the pyrolysis reactions are much less "clean" with the pectate L-arabinans. This may be associated with the fact that, in the pectates, a greater proportion of the L-arabinose occurs in the chain, rather than as pendant L-arabinofuranosyl groups. It is also probable that the galacturonan sectors of the pectates are decarboxylated and further pyrolyzed at relatively low temperature, as had been observed with uronic acids in wood[5]. The facile pyrolysis will produce materials which are likely to induce more complex modes of pyrolysis of the arabinoside units.

Compound **1** had previously been obtained in a yield of 2.3% by pyrolysis of L-arabinose[11]. The ^{1}H-n.m.r. spectrum of **1** in acetone-d_6 (see Tables III and IV) reveals that the molecule contains hydrogen bonding involving the hydroxyl proton of OH-3, probably an intramolecular hydrogen-bond with the furanose ring-oxygen space atom. The hydroxyl proton gives a doublet at 4.32 p.p.m. with a spin-spin coupling constant of $J_{OH,3}$ 5.1 Hz (see Tables III and IV); H-1 gives a broad singlet at 5.33 p.p.m. ($J_{1,2}$ ~0.1), H-5_{endo} a doublet at 3.56 p.p.m. and H-5_{exo} a doublet of doublets at 3.43 p.p.m., with the signal for H-3 obscured by the H-5 absorbances. The signals for H-2 and OH-2 occur at the same position, 3.75 p.p.m., as singlets. Disrupting the hydrogen bonding (by adding a drop of D_2O) changes the conformation of the molecule. The H-1 signal then appears as a doublet ($J_{1,2}$ 2.7 Hz), that of H-2 becomes a broad singlet with the area under the peak at 3.77 p.p.m. reduced by half (indicating the exchange of the OH-2 proton with deuterium), and the signal for OH-3 is eliminated. The ^{13}C-n.m.r. spectrum of **1** (see Table V) was assigned by comparison with similar spectra[12] reported. Acetylation of **1** was accomplished by standard means, to afford 2,3-di-*O*-acetyl-1,5-anhydro-β-L-arabinofuranose, and the ^{1}H-n.m.r. spectrum of this acetylated derivative agreed with earlier values[11].

The simplest assumption regarding the mechanism of formation of **1** is that it is derived from pyrolysis of the L-arabinofuranoside units in the hemicellulose and the pectic substance. By analogy with the known mechanism of pyrolysis of sucrose[12], it is probable that this occurs *via* the protonated form (**3**), and that the protons are derived from such other pyrolysis reactions as decomposition of acetic ester groups[5], or from uronic acids. The pyrolysis may proceed either *via* the inter-

TABLE IV

^{1}H-N.M.R SPIN–SPIN COUPLING CONSTANTS (Hz) FOR **1**

Solvent	$J_{1,2}$	$J_{3,OH-3}$	$J_{4,5exo}$	$J_{5exo,5endo}$	$J_{2,4}$
Acetone-d_6	~0.1	5.1	3.9	7.1	[a]
Acetone-d_6 + D_2O	2.7	none	3.4	[a]	sm[b]

[a]Could not be measured. [b]Seen as sharpening of one signal upon irradiation of the other.

TABLE V

^{13}C-N.M.R. VALUES[a] FOR **1**

C-1	*C-2*	*C-3*	*C-4*	*C-5*
100.55	84.17[b]	78.79	84.60[b]	65.79

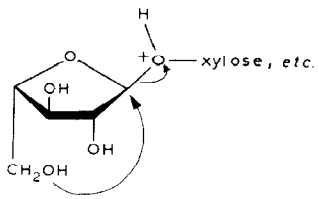
[a]In acetone-d_6 with Me_4Si as internal standard. [b]May have to be interchanged.

mediate L-arabinose cation **2** (analogous to the sucrose mechanism[13]), which undergoes 5⟶1 ring-closure, or, alternatively, may involve $SN2_{CB}$ attack of O-5 at C-1 in **3** as shown.

The type of procedure described makes possible the preparation of **1** in reasonable yield under mild conditions from readily avaiable, low-cost biomass. The residues from the procedure are relatively lightly degraded and might retain value for other purposes. Many other abundant sources of low-value biomass have high L-arabinan contents (*e.g.*, sugar-beet pulp, other cereal brans, etc.) and should be suitable for such treatment.

EXPERIMENTAL

Materials.— The corn bran was supplied by A. E. Staley Manufacturing Co. as "Staley Refined Corn Bran" with 0.6% of ash and 4–6% of starch. Orange peel



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was kindly provided by Dr. James H. Tatum of USDA Citrus and Subtropical Products Laboratory, Florida. It had been dried for 18 h at 85° in a forced-draft oven, and, on receipt, it was Wiley-milled to pass a 1-mm screen. The Ponderosa pine bark was collected from a healthy 49-year-old tree, and the phloem was immediately stripped from the outer bark, and both were air-dried overnight in the dark and then Wiley-milled to pass a 1-mm screen.

General methods.— Melting points were determined in a Fisher–Johns hot-stage, melting-point apparatus and are uncorrected. ^{1}H-N.m.r. and ^{13}C-n.m.r. spectra were recorded with a Jeol FX-90 instrument at 90 MHz and 22.5 MHz, respectively. All g.l.c. analyses were made on packed nickel columns (22 mm o.d. x 2.4 m), using nitrogen as the carrier gas, flame-ionization detection, and digital integration. Column packings used were (*a*) 3% of SE-52 on GasChrom Q (100–120 mesh) programmed from 130° to 250° at 6°/min for Me_3Si ethers and (*b*) 3% ECNSS on GasChrom Q (100–120 mesh, programmed from 160° to 190° at 2°/min for alditol acetates. The tar was derivatized for g.l.c. analysis by using bis(trimethylsilyl)trifluoroacetamide in pyridine, with D-glucitol as the internal standard. Thin-layer chromatography was conducted on Bakerflex IB2 plates in 1:2 chloroform–tetrahydrofuran (THF), with detection achieved by spraying with 5% sulfuric acid in ethanol followed by charring. Vacuum pyrolyses were conducted on a 0.3–3 g scale at 266 Pa, under a nitrogen flow (sufficient to decrease the vacuum by 133 Pa) as reported previously[14]. All samples were oven-dried for at least 30 min at 110° before pyrolysis.

Isolation and purification of **1**. — Three batches of corn bran (~2 g each) were pyrolyzed for 30 min at 300° and the tar fractions produced were combined. The entire amount of tar (1.81 g) was dissolved in the minimum amount of 1:2 $CHCl_3$–THF and eluted through a column (3.5 x 50 cm) of silica gel 60 (70–230 mesh) with 1:2 $CHCl_3$–THF. Fractions (~8 mL) were collected. The fractions shown by t.l.c. to contain the major product (R_f 0.42) were combined, and the solvents removed by rotary evaporation. The resulting oil crystallized from absolute ethanol, to give colorless needles, m.p. 74–76° (lit.[9] 76–78°).

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