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Note

Degradation of hemicelluloses by piperidine*

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Piperidine is a reactive nucleophile in carbohydrate displacement reactions[1–2], which opens cyclic carbonates[3], and reacts with monosaccharides[4], acetylated monosaccharides[5], and *O*-acetylglycosyl halides[3] to form glycosylamines. The initially formed glycosylamines undergo further reactions such as the Amadori rearrangement[6] and the non-enzymic Browning reaction[6,7].

When holocellulose from the bark[8] of loblolly pine (*Pinus taeda*) was treated with boiling piperidine, 33.2% dissolution occurred. This was not simply an extraction process but involved a chemical reaction between the solvent and the polysaccharide. This was evident from the high nitrogen content (8.27%) of the extraction product, and its weight which was 1.8 times that of the material lost from the holocellulose. These data indicate that the product derives from equal weights of piperidine and polysaccharide.

The source of the degraded material was determined by analyzing the carbohydrate composition of the holocellulose before and after extraction with piperidine. Samples were hydrolyzed and analyzed[9] as their silyl ethers by g.l.c. The results (Table I) indicate that fairly large proportions of glucose-, xylose-, and arabinose-containing polysaccharides were lost and smaller proportions of the galactose- and mannose-containing materials were decomposed. Most of the weight loss came from the hemicellulose fraction of the holocellulose, since treatment of wood cellulose with piperidine caused negligible weight losses.

The piperidine-soluble material from the holocellulose was dissolved in chloroform and differentially extracted by 10% hydrochloric acid and 5% aqueous sodium hydroxide to give basic (41.4%), neutral (21.7%), and acidic (1.5%) fractions. The molecular weight profile of each fraction obtained by high-pressure gel-permeation chromatography is shown in Fig. 1. The chromatogram shows a very broad range of molecular weights (<100–>900); the peak at 900 corresponds to the void volume of the column.

The formation of these polymeric materials could involve an initial nucleophilic displacement by piperidine at the glycosidic position of the polysaccharide. The

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TABLE I

COMPOSITION OF LOBLOLLY PINE HOLOCELLULOSE

	Before extraction[a] (%)	*After extraction*[a] (%)	*Loss* (%)
Arabinose	4.1	0.9	3.2
Xylose	9.4	2.5	6.9
Mannose	9.8	7.0	2.8
Galactose	6.7	4.7	2.0
Glucose	62.4	52.3	10.1

[a]Weight percentages of the sugars based on the unextracted holocellulose.

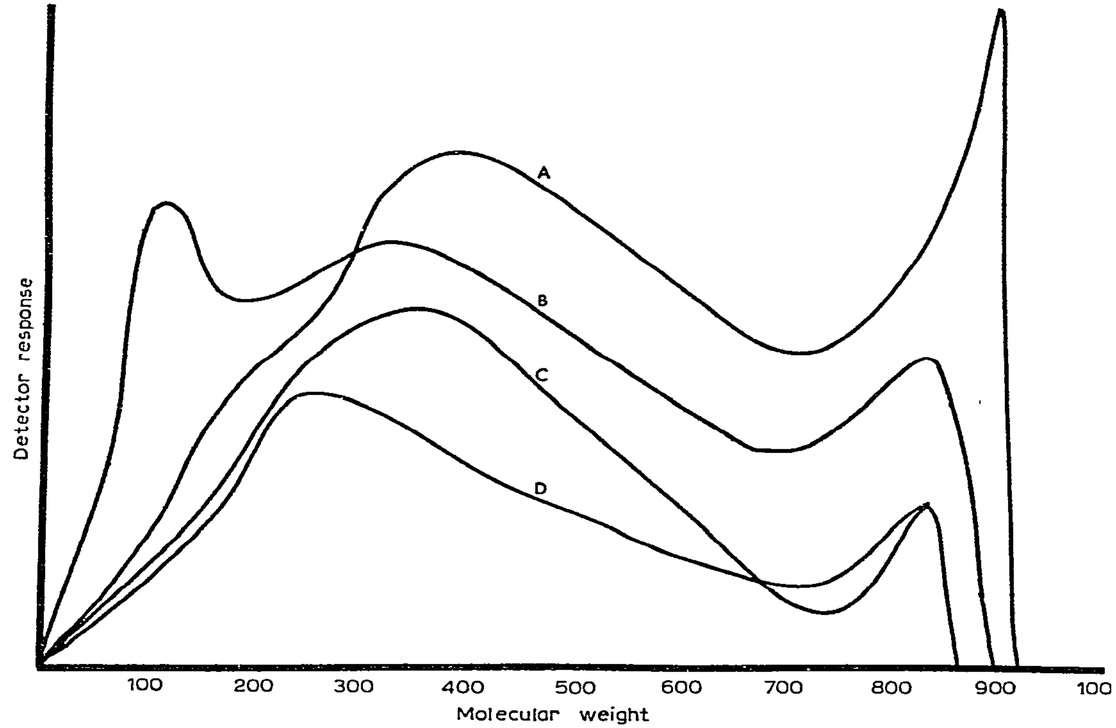

Fig. 1. Molecular weight profile of the neutral (A), acidic (B), and basic (C) fractions obtained by piperidine degradation of the bark holocellulose of *Pinus taeda*.

initially formed glycosylamine could be further degraded by rearrangement, dehydration, enolization, and polymerization. Earlier studies by Hodge and Rist on the piperidine derivatives (glycosylamines) of D-glucose and D-galactose indicated that these compounds readily underwent both the Amadori rearrangement and the non-enzymic browning reaction[4–7].

EXPERIMENTAL

Elemental analyses were performed by the Heterocycle Chemical Corp. (Harrisonville, Missouri). N.m.r. spectra were obtained by using a Jeolco minimar spectrometer. Tetramethylsilane was used as an internal standard. I.r. spectra were obtained with a Perkin–Elmer model 137 G spectrophotometer. G.l.c. was performed with a Perkin–Elmer model 900 gas chromatograph with a hydrogen-flame detector, a stainless-steel column (6 ft × 0.25 in. o.d.) packed with 5% SE-30 on Chromosorb W, a program temperature of 100–200° at 8°/min, and a helium flow-rate of 35 ml/min. Liquid chromatography was performed with a Waters Associates, Inc. Model 202-401 liquid chromatograph with a u.v. detector, a stainless-steel column (4 ft × 0.375 in. o.d.) packed with Poragel (60-Å column, Waters Associates, ≠26900), and chloroform as the elution solvent at 0.9 ml/min. D-Glucose penta-acetate, cellobiose octaacetate, and polypropylene glycol (Waters Associates, ≠41994) were used as standards for the calibration of molecular weight. The isolation and characterization of holocellulose from the bark of loblolly pine have been described[8].

A sample (10 g) of ground (60 mesh) holocellulose was treated with boiling piperidine (Soxhlet) for 7 days. The extraction product (Found: C, 59.06; H, 8.38; N, 8.27%) recovered on removal of the piperidine was dissolved in chloroform, and the solution was differentially extracted with 10% hydrochloric acid (basified and re-extracted into chloroform) and 5% aqueous sodium hydroxide (acidified and re-extracted into chloroform) to separate the extraction product into acid, basic, and neutral fractions. Each chloroform extract was washed with water, dried ($MgSO_4$), and concentrated at 50°.

The material (41.43%) (Found: C, 61.89; H, 8.01; N, 10.61%) extracted into acid had ν_{max}^{film} 3200, 2870, 1640 cm^{-1}; δ ($CDCl_3$) 1.60, 2.40, 3.40 p.p.m.

The material (1.25%) (Found: C, 61.19; H, 7.01; N, 5.15%) extracted into base had ν_{max}^{film} 3200, 2900, 1740, 1630 cm^{-1}; δ ($CDCl_3$) 1.23, 1.57, 2.00, 3.60, 3.76, 6.68, 7.20 p.p.m. The n.m.r. assignments were made after treating the extraction product with an ether–ethanol solution of diazomethane.

The neutral fraction (21.71%) (Found: C, 41.85; H, 4.20; N, 8.77%) had ν_{max}^{film} 3300, 2860, 1635 cm^{-1}; δ ($CDCl_3$) 1.12, 1.40, 3.27 p.p.m.

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