[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY,[2] FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Composition of Hemicellulose Isolated from Maple Wood[1]

BY R. L. MITCHELL AND GEO. J. RITTER

Hemicelluloses of varying degrees of solubility can be recovered from an aqueous alkali extract of plant materials by precipitation with alcohol. If the extraction is made on a lignocellulosic material, the precipitated hemicelluloses are contaminated with ligneous material, the removal of which involves a prolonged refining procedure.[3,4] Since the readily soluble hemicelluloses are lost during the preparation of Cross and Bevan cellulose and refined pulps, only the more insoluble hemicelluloses are extractable from those materials in a lignin-free condition. On the other hand, both the readily soluble and the more insoluble hemicelluloses are present in holocellulose,[5,6] and can be isolated easily in a lignin-free condition from this material by a combination of fractional extraction and fractional precipitation. In the present study hemicelluloses were isolated from a large batch of holocellulose prepared[7] from sugar maple wood. The yield of holocellulose was 74% of the extractive-free wood.

In this report the isolation, fractionation, composition, and approximate minimum molecular weight of the different hemicellulose fractions are considered. The identification of the constituents composing the hemicellulose fractions will be considered in a later report.

Preparation of Hemicellulose Fractions

Fraction I.—A water-soluble fraction of hemicellulose was prepared by extracting the holocellulose with 30 parts of boiling water for one hour. The filtrate was concentrated and the hemicelluloses were precipitated by slowly adding 95% alcohol while stirring, after which they were filtered off and designated as fraction I-B. This fraction constituted 3.0% of the holocellulose. The precipitate obtained by adding acetone to the filtrate of I-B is designated as fraction I-A. It constituted 1.6% of the holocellulose.

Fraction II.—The hemicellulose fraction was isolated by treating the insoluble residue from extraction I with 10 parts of cold 2% sodium carbonate solution for forty-eight hours. The dissolved material was precipitated with alcohol, filtered and freed from salts by suspending it in water, acidifying with hydrochloric acid, adding alcohol and acetone, and filtering. It constituted 2.2% of the holocellulose.

Fraction III.—A fraction soluble in 4.0% sodium hydroxide solution was prepared from the insoluble residue remaining after the removal of fraction II. It was extracted at room temperature by using 10 parts of the alkali solution to 1 part of the insoluble residue, and recovered by precipitating with alcohol, filtering, suspending the material in water, acidifying, precipitating with alcohol and acetone and filtering. It constituted 14.9% of the holocellulose.

Fraction IV.—A fourth fraction was prepared by treating the insoluble residue from extraction III with 10 parts of boiling 10% sodium hydroxide solution for one hour.[8] This fraction was recovered from the alkaline solution and purified in the same manner as fraction III. It constituted 3.5% of the holocellulose.

Approximately 25.0% of the holocellulose is included in the foregoing isolated hemicellulose fractions. In addition, approximately 4.0% of acetyl was removed from the holocellulose during the alkaline extractions, leaving 71% of the holocellulose or 52.5% of the wood remaining in the residue from extraction IV. Fractions I and II were exceedingly hygroscopic, so much so that they tended to become viscous on days of low humidity and dissolved in the moisture absorbed from the air on days of high humidity. The hygroscopic property was practically eliminated by repeated treatments with absolute alcohol and final washings with ether. Fractions III and IV are also hygroscopic but less so than the first two.

Analysis of Hemicellulose Fractions

The hemicellulose fractions were washed with alcohol and ether, dried at 80° in a vacuum oven, and then analyzed for uronic acids, pentosans, methoxyl and acetyl. Hexosans were determined by difference. The specific rotation and iodine number were also determined on each of the fractions. The results of the analyses are listed in Table I.

Uronic Acid Anhydrides.—Uronic acid anhydrides were determined by the hydrochloric acid method of Link.[9] Their highest concentration, 28.9%, is found in fraction II, which indicates that sodium carbonate has a selective solvent action on the acid-containing constituents. In the remaining fractions the uronic acids are most concentrated in the water-soluble hemicellulose and decrease with increasing concentration of the alkali solvent.

Pentosans.—Pentosans were determined by Tollens' method[10] and reported as xylan because it is the principal

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(2) Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

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pentosan in hardwoods. The xylan values in Table I have been corrected for the xylan equivalent of the furfural liberated from the uronic acids during the pentosan determination.[11] Xylan increases in concentration with decreasing solubility of the hemicelluloses, as is shown by comparing the values 46.1% in the most soluble fraction I-A to 80.9% in the least soluble fraction IV. The preceding results indicate that sodium hydroxide solutions are selective solvents for xylan.

Methoxyls.—Methoxyl determinations were made according to Clark's procedure.[12] The values vary between 2.1 and 2.7% for the different hemicellulose fractions. It is of interest to note that methoxyls and uronic acids are still present in fraction IV.

Acetyls.—Acetyls were determined by a modification of Clark's procedure.[13] The water-soluble fractions A and B contained 9.3 and 9.2% of the acid radicals, respectively. As would be expected, the acetyls are absent in the alkaline extracted hemicelluloses.

TABLE I

ANALYSIS OF HEMICELLULOSE FRACTIONS

Fraction No.	Yield, %[a]	Uronic acid anhydride, %[b]	Xylan, %[b]	Methoxyl, %[b]	Acetyl, %[b]	Hexosan (by diff.), %[b]	$[\alpha]_D$
I-A	1.6	17.1	46.1	2.7	9.3	24.7	−38
I-B	3.0	15.8	48.7	2.3	9.2	24.0	−25
II	2.2	28.9	54.7	2.6	...	13.7	−34
III	14.9	12.2	79.2	2.1	...	6.5	−70
IV	3.5	9.3	80.9	2.3	...	7.5	−83

[a] On basis of weight of the oven-dry holocellulose. [b] On basis of the weight of the oven-dry fraction.

Hexosans.—No attempt was made to identify the hexosans in this part of the study. They were determined by difference and appear to decrease with decreasing solubility of the hemicelluloses through fraction III and start to increase in fraction IV. Data on the identification of the hexosans will be reported in a succeeding paper on the hydrolysis products in the hemicellulose fractions.

Specific Rotation.—Specific rotations were determined on 1.0% solutions of the hemicelluloses in dilute sodium hydroxide solution. The first three cellulose materials manifest similar specific rotations ranging from −25 to −38°. In contrast the two sodium hydroxide soluble materials have rotations of −70 to −83°, respectively, which fall within the range of −65 to −96° specific rotations of hemicelluloses from hardwood reported by Doree.[14]

Approximate Minimum Molecular Weight of Hemicelluloses by Iodine Number Method.—The iodine number, defined as the number of cubic centimeters of 0.1 *N* iodine in alkaline solution used by 1 g. of material, is a measure of the aldehyde groups.[15] If it is assumed that the aldehyde is an end group, its measurement by the iodine number affords a means for calculating the minimum molecular weight of the hemicellulose. Oxidation of an aldehyde group by sodium hydroxide–iodine solution is represented by the equation

$$RCHO + I_2 + 3NaOH \longrightarrow RCOONa + 2NaI + 2H_2O$$

The gram molecular equivalent of iodine or 20,000 cc. of 0.1 *N* iodine solution is necessary to oxidize one aldehyde group in a gram molecular weight of material to a carboxyl. By assuming the presence of one aldehyde group per molecule, the minimum molecular weight of the hemicelluloses was calculated from the iodine number by the formulation: Molecular weight = 20,000/Iodine number.

The values for iodine numbers and the minimum molecular weights calculated from them for the hemicellulose fractions are listed in Table II. A comparison of the molecular weights obtained indicates that they follow the order of solubility in water for the different hemicellulose fractions. The four groups listed in the order of decreasing solubility in water are fractions I-A, I-B, II, and III, and possess molecular weights in the approximate ratio of 1:2:4:10.

TABLE II

APPROXIMATE MINIMUM MOLECULAR WEIGHT OF HEMICELLULOSE FRACTIONS CALCULATED FROM IODINE NUMBER

Fraction	Iodine no.	Minimum mol. wt.	Total no. of constituents and substituent groups	Approximate no. of constituents: Uronic acid anhydride	Xylan	Hexosan	Approx. no. of substituent groups: Methoxyl	Acetyl
I-A	18.6	1,070	10	1	4	2	1	2
I-B	8.9	2,250	20	2	8	3	2	5
II	5.2	3,830	28	6	16	3	3	...
III	1.9	10,500	81	7	63	4	7	...

From the molecular weights and the analytical data in Table I the approximate number of anhydro sugar residues and substituent groups per molecule in each fraction were computed.

Summary

Lignin-free hemicelluloses were isolated from maple holocellulose which contains both the readily soluble and more insoluble hemicelluloses. In the isolation of the hemicellulose fractions a procedure was used to extract the fractions in the order of decreasing solubility by employing increasingly stronger solvents. The hemicellulose fractions were found to be composed principally of xylan associated with varying amounts of uronic acid anhydride and hexosan. The readily soluble hemicelluloses had lower values than the more insoluble hemicelluloses for their minimum molecular weights calculated from their respective iodine numbers.

MADISON, WIS. RECEIVED APRIL 11, 1940

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