*Chemical Studies on Wood Hemicelluloses. I. On the Hemicellulose of Japanese Beech Wood. I**

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(Received September 8, 1956)

Introduction

Concurrently with the development of an improved type of chemical pulp has appeared the need for still more minute knowledge of the carbohydrates associated with wood cellulose1).

Generally speaking, more hemicelluloses, which are said to have undesirable influences upon the manufacture and qualities of viscose or acetate rayon2), are contained in the chemical pulp from deciduous wood than from coniferous. But the chemical structure of wood hemicellulose is not yet clear. The deciduous woods, for all that, have recently appeared to be used increasingly for the dissolving pulp in Japan, owing to unavoidable circumstances of natural sources.

This research was designed to find out a suitable method of analysing wood hemicellulose by paper chromatography; and the behaviour of hemicelluloses in Japanese beech wood (*Fagus crenata* Blume) during the pulping processes was analysed. The state of hemicelluloses in wood pulp was also investigated.

Experimental Results and Discussion

(1) Preparation of Samples.—Beech wood grown in Hokkaido was employed in the present study. The normal analysis is shown in Table I.

TABLE I

THE COMPOSITION OF THE JAPANESE BEECH WOOD

	(%)
Ash	0.55
Extract with alcohol-benzene	1.50
Lignin	22.76
Pentosan	19.86
Uronic acid	0.76
Total cellulose	54.80
α-cellulose	40.61
β-cellulose	6.74
γ-cellulose	7.45

a. Wood.—Sawdust (40 mesh) of the wood was air-dried.

b. Unbleached Pulp.—Chips of the wood were cooked by sulfite pulping process using calcium base.

Cooking liquor: total SO_2 7%, combined SO_2 0.8%, liquor ratio 1 : 5. Time to 100°C, 2; time from 100°C to 110°C, 2; time from 110°C to 140°C, three hours. Maximum temperature, 140°C; maximum pressure, 7 atm. Cooking time at maximum temperature, five hours.

The pulp resulting from the procedure was washed and air-dried. Cuprammonium viscosity:** 4.20.

c. Bleached Pulp at the First Step.—Fifty grams of the unbleached pulp were treated with 1665 ml. of water containing 5.65 g. of chlorine for an hour. After the bleaching, the sample was washed with water until the filtrate indicated no reaction with potassium iodide-starch test paper, and air-dried.

d. Bleached Pulp at the Second Step.—Thirty grams of the said pulp were secondly treated with 600 ml. of NaOH solution at 90–95°C for an hour. The amount of NaOH used was 7% of that of the pulp. The pulp was washed and dried. Cuprammonium viscosity, 4.24.

e. Bleached Pulp at the Third Step.—Sixteen gram of the pulp were subsequently bleached with 300 ml. of water containing 1 g. of NaClO and 0.1 g. NaOH at 50°C for four hours. Cuprammonium viscosity, 4.06.

(2) Analytical Procedure of Hemicellulose.—As the hemicellulose was not satisfactorily extracted with alkali directly from the wood3), holocellulose was prepared from each sample by Wise's method4).

About 4 g. of the holocellulose was mixed with 72% sulfuric acid at room temperature. After 17.5 hours, the solution was diluted with water to a concentration of 4% sulfuric acid, heated in a bath of boiling water, neutralized with barium carbonate using congo-red test paper and filtered. The filtrate was evaporated to 50 ml.

The component sugars in each hydrolysate of the sample were detected by paper chromatography.

As much work has been done on the paper

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* Read before the 9 th Annual Meeting of the Chemical Society of Japan on April 5, 1956 at Kyoto.

1) W. J. Polglase; "Advances in Carbohydrate Chemistry," Vol **10**, (1955), p. 283.

2) G. Jayme and U. Schench *Mell. Textilber.*, **31**, 153 (1950).

** Cuprammonium viscosity means the specific viscosity of the solution of 50 mg. sample in 100 ml. Schweizer's reagent at 20°C.

3) H. Sobue and A. Hatano, *J. Chem. Soc. Japan. Ind. Chem. Sec.*) **55**, 131 (1952).

4) L. E. Wise and E. K. Ratliff, *Anal. Chem.*, **19**, 459 (1947).

chromatography of carbohydrates[5], various solvents were tested to find the most suitable method for the present research. After many preliminary experiments, it became clear that the use of circular chromatograms which were reported by Buurman[6] would have certain advantages. R_f values of reference-sugars obtained are shown in Table II.

TABLE II

R_f VALUE OF REFERENCE-SUGARS

Solvent / Sugars	Butanol-acetic acid-water (4 : 5 : 1)	Butanol saturated with water	Phenol saturated with water	Butanol-pyridine-water (4 : 1 : 2)
Arabinose	0.46	0.15	0.58	0.41
Xylose	0.47	0.17	0.49	0.46
Glucose	0.38	0.10	0.40	0.36
Galactose	0.35	0.09	0.45	0.33
Mannose	0.44	0.15	0.47	0.40

(3) Composition of Beech Pulp Hemicellulose.—Referring to the results mentioned above, the chromatographic separations were carried out on a sheet of Toyo-Roshi No. 2 filter-paper with the solvent mixture of *n*-butanol-pyridine-water (4 : 1 : 2).

Aniline hydrogen phthalate in *n*-butanol was used as a spray to reveal the sugars[7]. In every case where a sugar was indicated by R_f value, the identity was established by running further chromatograms with reference-sugar spots. And each component sugar was analysed quantitatively according to Buurman[6]. The results obtained are shown in Table III.

TABLE III

COMPOSITION OF HEMICELLULOSE OF BEECH WOOD

	Xylan	Araban	Mannan	Uronic acid
Wood	19.7	1.0	0.1	0.76
Unbleached pulp	5.7	trace	trace	0.26
Bleached pulp at the 1st step	5.0	—	trace	0.44
Bleached pulp at the 2nd step	3.1	—	trace	0.49
Bleached pulp at the 3rd step	2.8	—	trace	0.58

Uronic acid is perhaps 4-O-methyl-D-glucuronic acid. Rhamnose was not found in the hemicellulose, which differs from that of European beech wood (*Fagus sylvatica*) reported by Aspinall et al[8].

It is found, as is shown in Table III, that the greater part of xylan is removed from the wood during the sulfite cooking. Oxidative bleaching is less effective for the removal of the remaining xylan than the alkali treatment. About 3% of xylan still remains in the final pulp, which is so-called resistant xylan.

Mannan is contained in the original wood in small amount, but a trace of it is found to remain still in the final pulp without being removed in each step of the pulping process.

Both xylan and mannan, having similar chemical structure to cellulose, are considered to exist not only in the amorphous but also in the crystalline region of cellulose.

Araban contained originally in small quantity in the wood is almost completely removed during the sulfite cooking and chlorine-bleaching.

Uronic acid, which is probably 4-O-methyl-D-glucuronic acid, is found to be ruptured during the sulfite cooking, but D-glucuronic acid is formed again in the subsequent oxidative treatments of the pulp. Koike[9] found that most of the carboxyl group is distributed in the outer secondary lamellae. The fact that two-thirds of the carboxyl group is removed during the sulfite cooking indicates that the cooking liquor penetrates tolerably into the cell walls.

It was found by electron microscopy that these bleaching reactions proceed topochemically***. At any rate, the hemicellulose consisting mainly of xylan, mannan and uronic acid was found to be contained in the beech wood pulp for all the bleaching reactions; further treatment is needed to remove the residual xylan and mannan from the wood cellulose.

It is a characteristic of wood hemicellulose that it is very firmly associated with cellulose. The studies of the molecular structure of the Japanese beech wood hemicellulose will be published in subsequent papers.

Summary

1. A suitable method of analysing wood hemicelluloses by paper chromatography was studied.

2. The behavior of hemicellulose in Japanese beech wood (*Fagus crenata* Blume) during the chemical pulping processes was studied; the state of the hemicelluloses in wood pulp was investigated.

The beech wood used in this work was generously provided by Dr. H. Okada of Kokusaku Pulp Ind. & Co. Ltd.

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[5] G. N. Kowkabany, "Advances in Carbohydrate Chemistry," Vol. **9**, 303 (1954).

[6] A. Buurman, *Text. Res. J.*, **23**, 888 (1953).

[7] S. M. Partridge, *Nature*, **164**, 443 (1949) ; S. Machida, M. Inano, This Bulletin, **28**, 630 (1955).

[8] G. O. Aspinall, E. L. Hirst and R. S. Mahomed, *J. Chem. Soc.*, **1954**, 1734.

[9] R. Koike and S. Nagatomo, *J. Tappi*, **9**, 375 (1955).

*** The results will be published elsewhere.