

## Chemical Studies on Wood Hemicelluloses. II. On the Hemicellulose of Ganpi Bast Fibres. I\*

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Wood hemicelluloses, which have generally undesirable influences upon the manufacture and qualities of chemical fibres, are said to have rather favorable effects on paper-making<sup>1)</sup>.

Cottrill<sup>2)</sup> investigated the bearing of hemicelluloses of wood pulp fibres on paper-making properties, and assented that the excellent character of Japanese hand-made paper could be attributed to the peculiar method of paper-making. The Japanese hand-made paper which has elegant and strong quality, is made in the traditional manner. Bast fibres of certain plants are used as the raw material and the extracted juice of various plant roots and barks are employed as sizing and dispersing agents<sup>3)</sup>.

The present investigation, therefore, was attempted to explain the behavior of hemicellulose during the processes of Japanese paper-making. The relation between the chemical characteristic of the hemicellulose and the paper-making properties of the fibres was also investigated.

### Experimental

1) **Sample.**—The bast fibres used in the present study were obtained from the Ganpi plant (*Wickstroemia sikokiana* Franch. et Sav.) grown in Simane Prefecture. Ganpi, a species of *Thymelaeaceae*, is a wild shrub growing widely in Japan, and the paper made from it is one of the most typical hand-made papers of Japan. The bast fibres removed from the plant stems were cleaned by removing the upper brown cork tissue and flawed parts, washed sufficiently with water, and dried.

2) **Process of paper-making.**—The bast fibres thus purified were boiled with a sodium carbonate solution, in which the concentration of sodium carbonate is 20% of that of the pulp, and

washed in a stream to remove the material formed by the reaction with alkali for two days. In the stream the fibres are also mildly bleached.

Next, the fibres were beaten for about an hour in a beater. The rotation of the beater-roll is about 150 r. p. m.; pulp concentration is about 3%. The degree of beating of the resultant pulp estimated with Schopper-Riegler's tester was 25. The paper was made from the pulp by the hand process in the usual manner of Japanese paper-making, using the mucilage of the Tororo-aoi plant<sup>4)</sup> as the dispersing and sizing agent.

3) **Chemical constituents of the fibres in the process of paper-making.**—The samples from the various stages of the process were analysed in the usual manner<sup>5)</sup>. The results obtained are shown in Table I.

4) **Hemicellulose of the Ganpi plant.**—Hemicellulose fractions were obtained by alkaline extraction of holocelluloses prepared from Ganpi bast fibres. These fibres finely chopped were extracted with benzene-ethanol, filtered and air dried prior to use. From this sample, holocellulose was prepared by Wise's method<sup>6)</sup>. Yield was 87.0%. Hemicellulose fractions were extracted from the holocellulose with sodium hydroxide solution. Successive extractions with the 5 and 16% solution for periods of an hour at room temperature yielded two fractions; these hemicellulose fractions were designated "5% extract" and "16% extract", respectively. The solid hemicelluloses were recovered from the alkaline solutions by pouring the latter into 4 volumes of ethanol containing sufficient acetic acid to adjust the pH to about 6.5. The flocculent precipitate was centrifuged, washed with ethanol and ether, and then dried in a desiccator.

The dilute solution viscosity of the water-soluble "5% extract" in distilled water was measured and a plot of the reduced specific viscosity against concentration is represented by the upper curve of Fig. 1. In the  $\eta_{sp}/c \sim C$  curve, a significant polyelectrolyte behavior of the hemicellulose is indicated. The lower curves of Fig. 1 are the  $\eta_{sp}/c \sim C$  curves for the hemicelluloses in 10% potassium hydroxide solution

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TABLE I  
 COMPOSITION OF BAST FIBRES OF GANPI PLANT

	Original raw bast fibre	Pulp after alkali-cooking	Pulp after wet beating	Paper
Moisture	13.90%	10.98%	11.39%	11.51%
Ash	1.84 "	1.86 "	1.29 "	1.57 "
Benzene-Ethanol extract	2.11 "	1.71 "	1.62 "	1.85 "
Cold water extract	2.84 "	2.68 "	0.81 "	1.97 "
Hot water extract	6.03 "	3.48 "	1.32 "	2.43 "
0.1% NaOH extract	15.54 "	4.46 "	3.74 "	5.49 "
Lignin	3.30 "	2.77 "	2.80 "	2.89 "
Uronic acid	16.36 "	7.60 "	4.46 "	2.08 "
Total cellulose	61.56 "	81.46 "	82.19 "	84.30 "
$\alpha$ -Cellulose	60.89 "	65.32 "	63.91 "	63.25 "
$\beta$ -Cellulose	17.47 "	20.56 "	21.84 "	22.48 "
$\gamma$ -Cellulose	11.64 "	14.12 "	14.25 "	14.27 "
Pentosan	21.62 "	18.37 "	16.02 "	14.15 "
Copper value	1.33	1.16	0.84	0.59
Degree of polymerisation	—	1832	1688	1397

at 30°C. Intrinsic viscosities of the hemicelluloses in 10% aqueous potassium hydroxide were determined from these curves, and the degree of polymerisation was calculated by using the relation<sup>7)</sup>  $[\eta] = 4.4 \times 10^{-3} \times (D.P.)$ . The component

solvent, and *o*-aminodiphenyl reagent<sup>8)</sup> as a spraying reagent. The hemicelluloses were found to be mainly composed of D-xylose and D-glucuronic acid and of small amounts of D-mannose, D-galactose, L-arabinose and L-rhamnose. The chromatogram shows that the uronic acid is partly presented as 4-O-methyl-D-glucuronic acid. Data obtained are shown in Table II.

 TABLE II  
 COMPARATIVE DATA FOR HEMICELLULOSE  
 FRACTIONS ISOLATED FROM GANPI HOLO-  
 CELLULOSE

Fraction	Yield <sup>a)</sup> (%)	Degree of polymerisa- tion <sup>b)</sup>	Uronic anhyd- ride <sup>c)</sup> (%)	Xylan <sup>c)</sup> (%)
5% extract	18.0	157	15.8	80.9
16% extract	7.3	160	13.6	58.1

a) Expressed as percentage of extractive-free bast fibres and corrected for moisture and ash.

b) Calculated as a pentosan.

c) Corrected for moisture and ash.

### Discussion

As is shown in Table I, substances other than cellulose are contained in the bast fibres of the Ganpi plant than in wood pulp fibres. In the paper-making processes mentioned above, these substances are still retained without much injury.

Especially, it is noticeable that much hemicellulose is kept in the fibres. The hemicellulose extracted from the bast fibres with aqueous sodium hydroxide is mainly composed of D-xylose and D-glucuronic acid (which may be partly present as 4-O-methyl-D-glucuronic acid),

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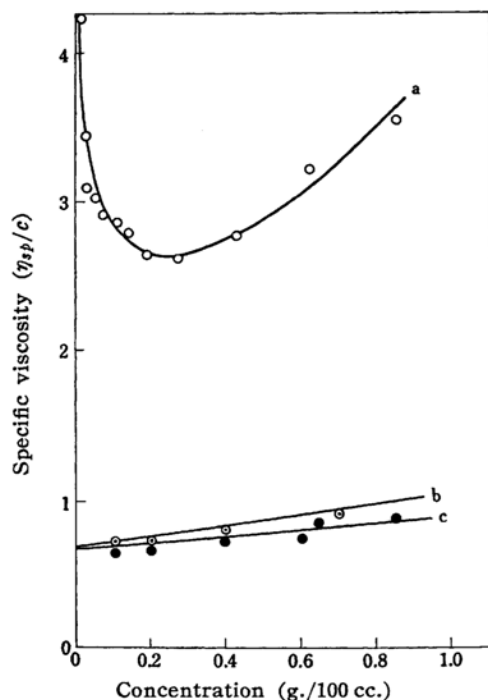


Fig. 1. Plot of viscosity against concentration for 5% extracted hemicellulose in water (a), and 5% and 16% extracted hemicellulose in 10% potassium hydroxide solution (b and c respectively).

sugars of the hemicelluloses were analysed chromatographically in the usual manner, using butanol-pyridine-water (6:4:3 by volume) as a

and it contains also small quantities of D-mannose, D-galactose, L-arabinose and L-rhamnose. The analytical data are interesting with regard to the fact that a polysaccharide containing D-galacturonic acid was found in the water-extract of the Ganpi bast fibres<sup>9</sup>. The polysaccharide is removed in the course of the preparation of holocellulose and hemicellulose. As is shown in Table II, the average degree of polymerisation of each alkali-extracted fraction of hemicellulose calculated as a pentosan is about 160. The fractions contain 15.8% and 13.6% uronic anhydride, which correspond to one carboxyl group for each six and eight pentose sugar units respectively. It is found that the hemicellulose molecule has a linear structure and the uronic groups are present along the polymer chain, because the hemicellulose indicates typical polyelectrolyte behavior in the solution. Although a great part of the uronic residue in the fibres is removed in the paper-making processes, it is found that a few percent of the uronic residue still remains in the hand-made paper.

The contents of total cellulose in the bast fibres increase naturally in each paper-making process. In the beating process, a part of  $\alpha$ -cellulose depolymerizes to  $\beta$ -cellulose; this depolymerization of cellulose is also proved from the degree of polymerization. Nevertheless, the degree of polymerisation of the Ganpi cellulose is kept higher not only than wood pulp but also than Mitsumata fibres<sup>10</sup>.

It is due to the presence of a great quantity of hemicelluloses that the long bast fibres are rendered so amenable to the wet beating process in a beater, by being fibrillated rather than cut or tangled. The hemicelluloses which are strongly hydrophilic polyuronides make also the fibres and fibrils to be more plastic, and tend to increase the areas of intimate contact between these elements, when they are felted to form a sheet of paper. Further, the hemicelluloses, cooperating with the plant mucilage employed, cause the fibres to be well dispersed in water to accomplish a good distribution of fibres in the fibre mat. Both these effects of the hemicelluloses increase the strength, transparency, density, softness and grease-proofness of the paper produced. This view would be proved, for example, by

Leech's experiment<sup>11</sup>) in which locust bean gum was employed in the beating of wood pulp for the sake of increasing the strength of the paper made from the pulp. But Jayme<sup>12</sup>) assents that the quality as well as quantity of hemicellulose present in the fibres is of importance in attaining strength in paper made from pulp. Limeric and Corey<sup>13</sup>) said that the hemicellulose containing many uronic acids is of advantage for the production of strong papers. The hemicellulose molecule of Ganpi bast fibres has comparatively long linear structure, and is strongly hydrophilic on account of the presence of uronic acid residue along the molecular chain. This fact has probably a significant bearing on the character of Japanese hand-made paper. It is considered to be necessary to investigate the question further to find a complete picture of the chemical nature of Ganpi hemicellulose.

### Summary

The composition of the bast fibres of Ganpi plant (*Wickstroemia sikokiana* Franch. et Sav.) was investigated in the processes of the traditional paper-making of Japan. It was found that hemicelluloses of the bast fibres had significant bearings on the paper-making and the excellent character of Japanese paper.

The hemicellulose isolated from holocellulose of the Ganpi bast fibres by alkaline extraction were found to be composed of 13.6~15.8% of D-glucuronic acid (which is partly present as 4-O-methyl-D-glucuronic acid), 58.1~80.9% of D-xylose, and small amounts of D-mannose, D-galactose, L-arabinose, and L-rhamnose. It was shown that the degree of polymerisation of the hemicellulose calculated as a pentosan is about 160, and the molecule has basically a linear structure in which the uronic groups are present along the polymer chain at a ratio of one carboxyl group for each six or eight pentose sugar units.

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