HIGHLY PURIFIED CELLULOSE FROM JUTE FIBRE

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(Received June 16, 1966)

Cellulose was prepared from jute-fibre (*Corchorus olitorius*) purer than any previously reported. A combination of steps was used for pure cellulose preparation, each of which is separately employed in various cellulose industries.

The purest pulp was exceptionally white and had a comparatively high viscosity. The xylose and 4-*O*-methyl-D-glucuronic acid contents were so low that it may be concluded that these impurities are not chemically combined with cellulose but are probably present as difficultly removable impurities or incrustation. The difficulty in removing the last traces of 4-*O*-methyl-D-glucuronic acid as well as xylose from the purest pulp supports the hypothesis that these two substances are chemically combined, but not with the cellulose.

Introduction

It is desirable to produce pulps which are as nearly pure cellulose as possible especially for the production of certain cellulose derivatives. Normal purifying techniques always leave a small quantity of hemicellulose with the cellulose.

The great difficulty of removing all the mannan and xylan by any means which does not disrupt the cellulose chains themselves has led to speculate that anhydromannose and anhydroxylose units might be an integral part of the wood cellulose molecule. The resistance of mannan and xylan to removal from wood pulp by such drastic reactions as nitration, xanthation, hydrolysis lent support to the chemical bond concept. Centola [1] was not able to separate completely the nitrates of other carbohydrates from cellulose nitrate and concluded that the non-glucose sugars to some extent form part of the molecular chains of cellulose. Das, Mitra and Wareham[2] isolated a glucose-xylose-arbinose compound from cotton alpha-cellulose and concluded that these units were present in the cellulose structure as mixed crystal. Sarkar and co-workers[3] have refuted the possible existence of mixed crystal in jute alpha-cellulose on the ground that xylan-free material can be prepared by treating isolated holocellulose with 9.3% caustic soda solution. More recent works[4] have, however, failed to lend any support to the observation made by Sarkars and others. The presence of these non-cellulosic constituents according to the observation of Leech,[5] Rapson,[6] and Timell[7] is due to the sorption and tenacious retention of these substances by alpha-cellulose. Support for this fact came from the work of Yllner and Enstrom.[8]

According to this theory hemicelluloses are believed to be relatively short chain compounds, the mannose and xylose units of which have a pyranose structure and which therefore occupy longitudinally the same space as the anhydroglucose units in the cellulose chains. These hemicelluloses would be expected to pack readily into the oriented cellulosic structure and would be retained by lateral forces as in the case of secondary valency bridges normally found between adjacent cellulose chains.

Sarkar and others[9] have been able to isolate xylan-polyuronides complex from jute constituting the major portion of the hemicelluloses. This complex is of the glucurono-xylan type and according to Das Gupta and Sarkar[10] possesses a structure in which 3-*O*-methyl-glucuronic acid residue is present as a side chain at position 3 of the main xylose frame-work. More recently Srivastava and Adams[11] as well as Aspinall and Das Gupta [12] have shown that the branching of the main xylan chain occurs at position 2 with 4-*O*-methyl-D-glucuronic acid and not at position 3 as suggested by the previous workers.

During recent years with the ever increasing demand for cellulose products there has been a great urge to search for new raw materials and to develop new techniques for the purification of cellulose. Straws, bagasse and other such materials which are produced in a short period are getting preference for their use as raw materials where wood is not available. It is with this idea that an investigation was undertaken to see if the cellulose of jute is the same as hard wood and soft wood.

Experimental

A. Raw Material.—The jute used was *Corchorus olitorius* commonly known as the tossa variety. It was available from the local market, dust and other impurities were removed by hand picking. It was then cut into small pieces of 6–7

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cms in length and the moisture content was determined.

B. Chlorination.—Four hundred grams of moisture free jute-fibre was weighed out, was then soaked in 10 litres of tap water overnight and the required amount of chlorine was added at 1.9% consistency. The reaction was allowed to proceed for 2 hours at 18°C after which the amount of unconsumed chlorine was determined as usual. The sample was the ncentrifuged and the moisture content determined.

C. Caustic Extraction.—The wet pulp obtained after the chlorination process was extracted with 15% hot sodium hydroxide solution at 95°C for 3 hours at 6% consistency. At the end of the reaction the whole mass was diluted with cold tap water and mixed with a stirrer. It was then filtered, washed and pressed to remove the excess water.

D. Bleaching with Chlorine Dioxide.—The alkali extracted pulp was then bleached with 2% chlorine dioxide for 3 hours at 70°C at 6% consistency at pH 6 (buffered with pot. dihydrogen phosphate and alkali). The unconsumed chlorine dioxide was determined as usual. The resultant pulp was then washed with sulphur dioxide water, finally with water. The pulp was made into sheets for analysis. In one set of experiments the resultant pulp was not dried but centrifuged and stored to acquire uniform moisture content.

E. Final Caustic Treatment.—The effect of cold caustic soda solution at 25°C of different concentration was studied with the fully bleached pulp. Two sets of experiments were carried out, one with the dried and the other with the wet pulp.

F. Analytical Procedure.—Pulp hydrolysis and microanalytical procedure. One and a half gram of bone dry sample was treated with 15 ml 72% H_2SO_4 (sp. gr. 1.64) for 4 hours at room temperature (40 mesh Wiley-milled pulp). The sample was then stirred as required to effect solution of the pulp. Four hundred and eighty millilitres distilled water was then added and the solution was boiled under reflux for 4 hours at atmospheric pressure. After cooling, the solution was neutralized with stirring with freshly washed Amberlite I.R. 45 ion exchange resin until pH 4 was obtained. The sample was then separated from the ion exchanger by filtering through a sintered glass funnel, the exchanger being quantitatively washed with 300 to 400 ml distilled water.

The resulting solution was adjusted to pH 3 to 4 with glacial acetic acid and concentrated to approximately 10 ml by evaporating *in vacuo.* Phenyl mercuric acetate (I ppm) was added as a sugar preservative.

The chromatogram was developed in an n-butanol: pyridine: water=5:3:3 (V/V) solvent using the descending solvent technique with the machine direction of the paper perpendicular to the solvent front. The colour of the chromatogram was developed with 2-aminobiphenyl solution in a mixture of glacial acetic acid and phosphoric acid as usual. The colour and size of the unknown spot was compared visually with the known concentration of sugar samples until it was bracketed between two known concentrations of sugar.

G. Brightness and Colour Reversion.—Sheets were made from pulp according to TAPPI 217m-48 and the brightness measured on a DU spectrophotometer at 457m microns with reflectance attachment before as well as after aging for 18 hours at 105±0.5°C as usual.

H. Alpha-Cellulose of Pulp.—These determinations were made according to TAPPI 203m-58.

I. Copper Number.—These determinations were made according to TAPPI 215m-50.

J. Viscosity.—These determinations were made according to TAPPI 230m-50.

Discussion

The alpha-cellulose content of jute fibre is 57-62%.[13] The yield of 62.5% pulp indicates that the chosen conditions did not give rise to abnormal loss during pulping. The α-cellulose content of the prepared pulp was estimated to be 88.5% i.e. 55.3% on the basis of the jute fibre. This slight loss may be due to the peeling off reaction. Thus it seems that there is not much degradation during the pulping process.

The copper number of the pulp is 0.245 which also supports the fact that there is very little degradation during the pulp preparation. Finally the cupri-ethylenediamine viscosity of the pulp at this stage showed that it was in a relatively undegraded state (viscosity = 31.8 c/s.). Thus the chosen conditions of time, temperature and concentration were adequate for good delignification.

The brightness of the pulp was found to be 89.5% G.E. This brightness seemed to be one of the highest figures in the case of jute pulp. Whiteness and colour stability of the pulp were exceptional as was shown by aging (brightness = 84.3% G.E.) the pulp for 18 hours.

Chromatographic analysis of the pulp hydrolysate showed that it contained a relatively large amount of hemicelluloses, i.e. 2.02% xylose and 0.35% 4-*O*-methyl-D-glucuronic acid. No mannose nor any other pentose sugar was detected in the pulp hydrolysate. The resulting pulp on treatment with cold caustic soda at various concentrations lowered the xylose and 4-*O*-methyl-D-glucuronic acid contents to 0.55% and 0.1% respectively. With the increasing concentration of caustic soda up to 16%, there was no proportionate decrease in xylose or 4-*O*-methyl-D-glucuronic acid content. Similar observations were made in case of wood pulp by other workers.[6]

On treatment of the acid refluxed pulp with cold caustic soda solution, the xylose and 4-*O*-methyl-D-glucuronic acid contents were lowered to 0.1% and 0.05% respectively. The resulting pulp had a very low viscosity, about 1/6 the original value which showed that the pulp had been degraded much. As expected, however, lowering the degree of polymerization of the pulp simultaneously decreased the % yield obtained from these extractions.

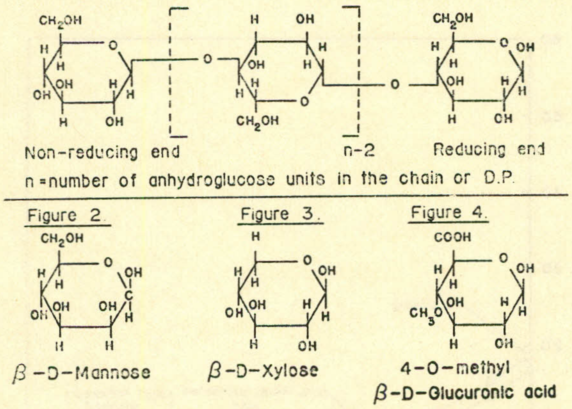

Fig. 1.

On extracting the dried as well as the moist pulp under the same experimental conditions, the dried pulp was found to contain 0.65% xylose and 0.13% 4-*O*-methyl-D-glucuronic acid, whereas the wet pulp contained 0.55% xylose and 0.1% 4-*O*-methyl-D-glucuronic acid respectively.

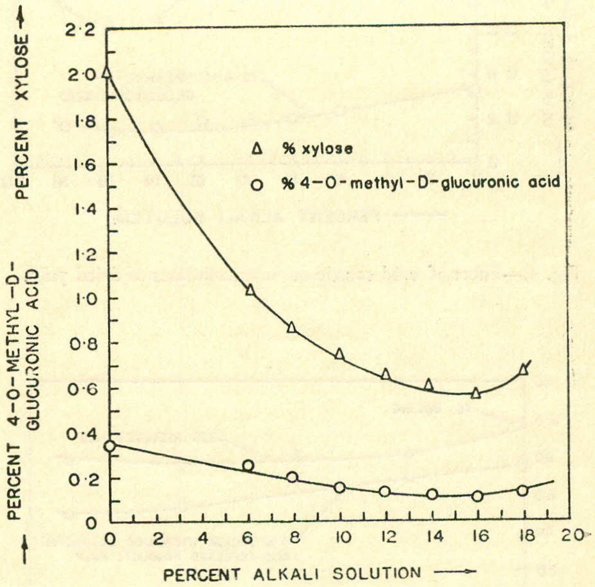

Fig. 3.—Effect of cold caustic on hemicelluloses of wet pulp.

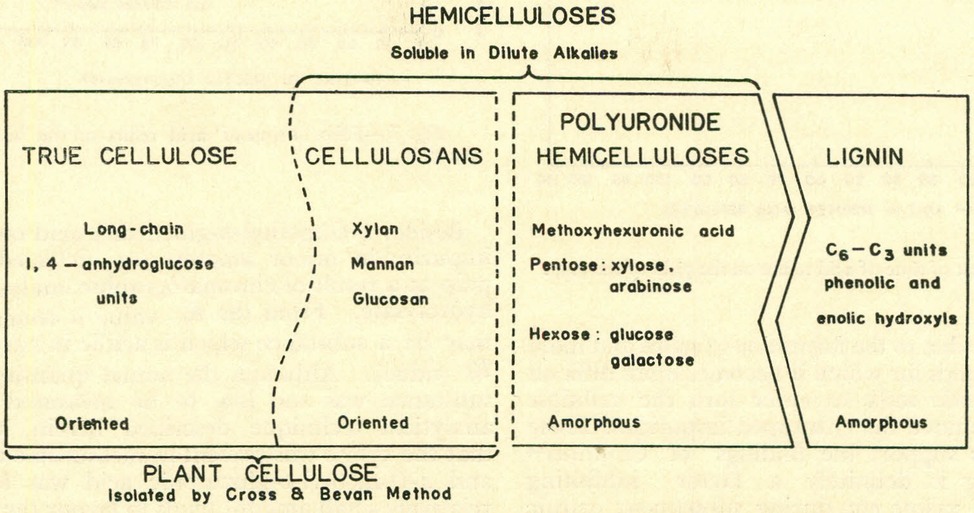

Fig. 2.—Diagram illustrating relationship between major cell-wall constituents.

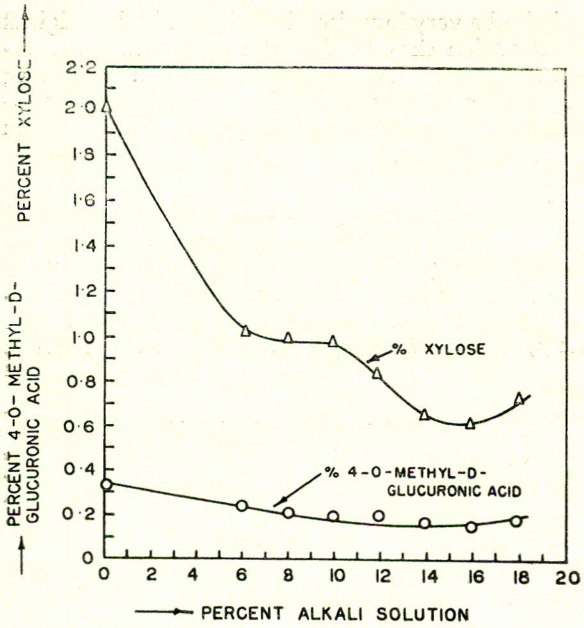

Fig. 4.—Effect of cold caustic on hemicelluloses of dried pulp.

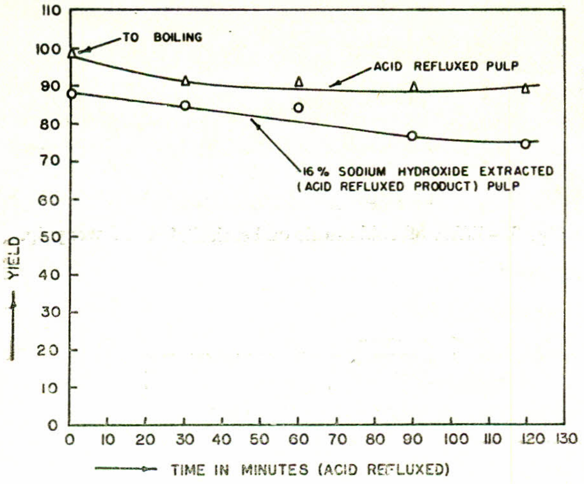

Fig. 5.—Effect of time of acid reflux on the yield of the plup.

This may be due to the formation of more and more hydrogen bonds for which it becomes more difficult for the caustic soda to enter into the cellulose matrix to remove the entrapped impurities. These observations support the findings of Couninis[14] that drying is definitely a factor inhibiting removal of xylose etc. during subsequent caustic extraction due to "hornification".

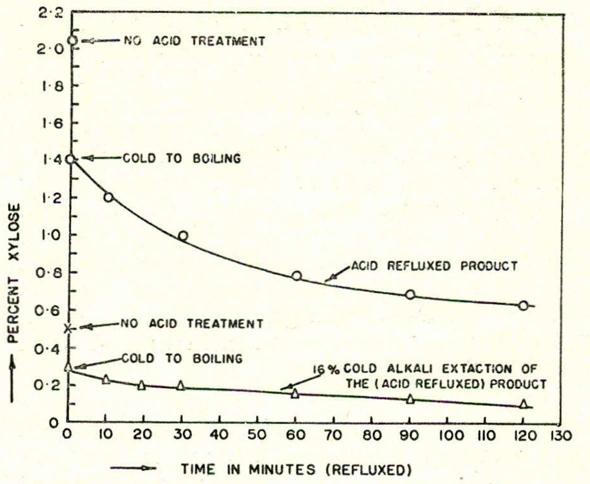

Fig. 6.—Effect of time of acid reflux on xylose content.

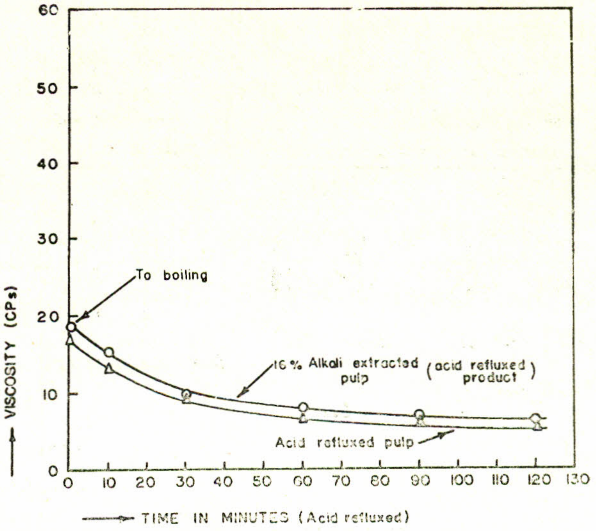

Fig. 7.—Effect of time of acid reflux on the viscosity of the pulp.

Besides 4-*O*-methyl-D-glucuronic acid one other impurity in minor amount was detected in the pulp as a result of chromatographic analysis of the hydrolysate. From the R_f value it seems that it may be a substance which is acidic in nature (low R_f value). Although the actual quantity of this substance was too low to be measured by the analytical technique described herein, the fact that the xylose was present in measurable amounts and 4-*O*-methyl-D-glucuronic acid was found in relatively small amount tends to favour the concept that the acid is linked as a side chain to a xylan

TABLE 1.—EXTRACTION OF REFINED PULP WITH SODIUM HYDROXIDE SOLUTION. (EFFECT OF COLD CAUSTIC ON HEMICELLULOSES OF WET PULP).

Alkali solution (% w/v) ..	0	6	8	10	12	14	16	18
Yield (%)	100	90.1	89.0	87.9	87.1	87.0	86.5	87.0
Brightness (% G.E.) (Before aging)	89.5	89.1	—	—	89.5	89.4	89.5	89.5
Brightness (% G.E.) (After aging	84.3	84.3	—	84.3	84.3	84.4	84.4	84.4
Viscosity (c/s)	31.8	31.6	31.3	31.3	29.5	24.8	24.8	24.3
% Xylose	0.02	1.01	0.85	0.75	0.65	0.60	0.55	0.65
% 4-*O*-methyl-D-glucuronic acid	0.35	0.25	0.20	0.15	0.15	0.12	0.10	0.12
Ratio of 4-*O*-methyl-D-glucuronic acid to xylose	5.7	4.0	4.2	5.0	4.3	5.0	5.5	5.4

TABLE 2.—EFFECT OF COLD CAUSTIC ON HEMICELLULOSES OF DRIED PULP.

Alkali solution (% w/v) ..	0	6	8	10	12	14	16	18
Yield (%)	100	90.4	89.8	88.5	87.5	87.3	86.8	87.2
Brightness (% G.E.) ..	89.5	89.4	89.5	89.5	89.5	89.6	89.6	89.6
% Xylose	2.02	1.05	1.01	1.01	0.85	0.65	0.65	0.75
% 4-*O*-methyl-D-glucuronic acid	0.35	0.27	0.22	0.22	0.20	0.17	0.13	0.15
Ratio of 4-*O*-methyl-D-xylose	5.7	4.0	4.6	4.6	4.2	4.0	5.0	5.0

TABLE 3.—ANALYSIS OF THE PULP AFTER REFLUXING WITH ACID (N/2 H_2SO_4).

Time of reflux (minutes)	Yield (%)	Viscosity (c/s)	Xylose (%)	4-*O*-methyl-D-glucuronic acid (%)	Ratio of xylose and acid
0	100	31.8	2.02	0.35	5.7
Cold to boiling ..	98.5	16.5	1.4	0.30	4.7
10	—	13.1	1.2	0.25	4.8
30	91.5	8.78	1.0	0.20	5.0
60	90.4	6.50	0.8	0.15	5.3
90	89.5	5.90	0.7	0.13	5.33
120	89.0	5.17	0.65	0.10	6.5

TABLE 4.—16% COLD ALKALI EXTRACTION OF THE ACID REFLUXED PULP.

Time of reflux (minutes)	Yield (%)	Viscosity (c/s)	Xylose (%)	4-*O*-methyl-D-glucuronic acid (%).
0	86.5	24.8	0.55	0.10
Cold to boiling ..	86.2	18.5	0.30	<0.10
10	86.0	15.1	0.21	<0.10
30	85.6	9.5	0.20	<0.10
60	84.6	7.7	0.17	<0.10
90	76.8	6.5	0.15	<0.10
120	74.8	5.5	0.10	<0.05

backbone. It is observed that after each treatment of cold caustic on wet pulp as well as the dried pulp, the weight ratio of 4-*O*-methyl-D-glucuronic acid to xylose in the residue is about 1:5, i.e. molar ratio of about 1:7 (Tables 1 and 2). This same ratio was also found in all the pulp hydrolysate after refluxing the pulp with N/2 H_2SO_4. From the fact that the concentration of these constituents in alkali extracted residue after acid reflux is too small to be measured by the analytical technique and that the slight variation in this ratio may be due to the experimental error, it may, however, be concluded that in the case of jute 4-*O*-methyl-D-glucuronic acid is chemically combined with xylose in about 1:7 molar ratio and it is this compound which has been removed by treatment with cold alkali.

As far as we are aware, this is the first time that a substance containing one 4-*O*-methyl-D-glucuronic acid group for seven xylose groups has been shown to be present in jute and to be very difficult to separate from the cellulose.

The results put forward in this investigation support the hypothesis that probably the hemicelluloses do not form an integral part of the cellulose in the case of jute fibre and that if they do form an integral part of the cellulose chain, it can only be an extremely small fraction.

Conclusion

Cellulose has been prepared from jute fibre (*Corchorus olitorius*) in a relatively high yield containing only 0.55 xylose and 0.1% 4-*O*-methyl-D-glucuronic acid. The product is still fibrous in nature and had a high viscosity indicating good retention of cellulose molecular chain length.

It is, therefore, concluded that cellulose molecule in jute fibre does not contain anhydroxylose and anhydromannose units as integral parts, but are retained as impurities intimately associated with cellulose which cannot be easily separated. If they do form an integral part of cellulose molecule, the amount so combined is extremely small as compared to the amount originally present. The ratio of 4-*O*-methyl-*D*-glucuronic acid to xylose removed is very close to 1:7 for each case. This is a good evidence that they are combined in about this ratio and it is this compound which was removed by the extraction.

It can be concluded that by extractive technique jute pulp can be purified to leave a fibrous residue of high molecular weight which is essentially pure cellulose containing only anhydro-glucose units as is the case with wood pulp.

Acknowledgement.—The author wishes to express his gratitude to Professor W.H. Rapson, Department of Chemical Engineering, University of Toronto, Canada, for his kind supervision in carrying out this work.

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