68. HEMICELLULOSE PREPARATION AND CHLORINATION CELLULOSE

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It has recently been shown that the use of boiling alcoholic-NaOH pretreatment of wood as a preliminary to hemicellulose extraction results in a marked destruction of furfuraldehyde-yielding materials [Preece, 1940]; the extent of the destruction is such as to make the use of this pretreatment undesirable, even though it may reduce the lignin contamination of subsequent hemicellulose preparations. At the same time, some polyuronide material may pass into the alcoholic extract [see, e.g., Preece, 1931]. The nature of this material has hitherto been obscure, though there has been little reason to suppose that it differed greatly from hemicelluloses prepared by more normal means of extraction. The preparation of the so-called 'lignosaccharide' has now been studied in some detail and, as will appear, it is clear that it does not represent a special type of cell-wall constituent.

Hemicellulose nomenclature has been extremely confused, and it seems that any mention of these substances should be accompanied by a precise definition of what is intended. The position has been reviewed by Norman [1937], who emphasizes that material passing into hemicellulose preparations has a double origin. There is reason to suppose that the 'crude cellulose' remaining after alternate chlorination and sulphite treatment of plant materials represents the essential structural material of the tissues present; it is regarded as comprising 'pure' cellulose with associated cellulosan, the latter in hard-woods appearing to consist very largely of xylan. A variable proportion of this xylan is soluble in dilute NaOH, as is also a proportion of glucosan material. Whether this readily soluble glucosan should be regarded as cellulosan is not clear. Again, the crude cellulose is associated with encrusting materials which are removed by chlorination. These encrusting materials also are soluble to a greater or less degree in dilute alkali and so contribute pentosan, uronic anhydride and possibly in some cases hexosan to the hemicellulose. If this view is correct, therefore, the mixed nature of hemicellulose preparations can hardly be contested, and further evidence that the preparations are mixtures is presented below. It might be suggested that the term hemicellulose should be reserved for the encrusting urono-polysaccharides, the cellulosans being regarded merely as part of the true native cellulose. However, it is perhaps too soon to endeavour to define the various types rigidly and, in general, Norman's tentative nomenclature will be followed, hemicellulose implying urono-polysaccharide material soluble in dilute alkali, irrespective of its origin, though excluding pectin and materials capable of extraction with water.

EXPERIMENTAL

Of the two wood samples used, the mahogany sawdust was from a commercial timber. The willow material used was from two 5-6-year-old branches cut from a growing tree, the tissues down to the wood being removed and dis-

carded before preparation of the sawdust; in this case, a period of some 3 months elapsed between the cutting from the tree and the preparation of the analytical material.

Alcoholic-NaOH extraction

The mahogany material was extracted successively with ether, 95 % ethyl alcohol, 0.5 % ammonium oxalate solution and 95 % alcohol, each extraction being carried out at boiling temperature for 1 hr. and being followed by appropriate washings on a cloth filter. The loss of dry matter was 8.96 %. A modified and probably more efficient pretreatment of the willow sawdust involved successive extractions with 95 % alcohol, 0.5 % ammonium oxalate solution (twice), distilled water and 95 % alcohol (twice), each extraction being for 1 hr. as before; the dry weight loss was 5.77 %. It may be noted that the willow material used all passed a 20-mesh sieve; the mahogany was used as received. The following treatments and determinations were carried out on the air-dried pre-extracted materials:

(a) Furfuraldehyde was determined directly on 0.5–0.7 g. of the prepared wood, the distillation being made in presence of 25 ml. each of *N* NaOH and *N* HCl.

(b) A similar weight of the wood was extracted with 100 ml. of boiling *x* % ethyl alcohol-1 % NaOH for 1 hr. The NaOH was neutralized by adding 25 ml. *N* HCl, and the alcohol was removed *in vacuo*. Furfuraldehyde determination was carried out after the necessary adjustment of volume. The values of *x* used were successively 10, 30, 50, 70 and 90 %.

(c) Extractions were carried out as in (b), the mixture then being filtered at the pump and the wood residue washed (using small portions of liquor for each wash) with (i) 50 ml. of liquid having the same composition as that used for extraction, and (ii) 75 ml. of aq. alcohol of the same concentration as that already used. The residue was transferred to the distillation flask and 25 ml. each of *N* NaOH and *N* HCl were added, furfuraldehyde distillation then being proceeded with.

(d) Owing to absorption of alkali by the wood, the 25 ml. of *N* HCl added in (b) did not give a neutral mixture. Since the figures obtained for 'extract' (b)–(c) were somewhat anomalous with the 70 and 90 % alcoholic treatments, it was suspected that this might be due to a loss of furfuraldehyde during the vacuum distillation, as a result of the somewhat acid conditions prevailing. Accordingly, samples of wood were refluxed with 100 ml. of alcoholic-NaOH as in (b), and the cooled mixture was titrated with *N* HCl by the conductometric method. Assuming that the titre required was *y* ml., addition of HCl was continued to 25 ml.; (25–*y*) ml. of *N* NaOH were then added, the further treatment being as in (b). This treatment was applied only to willow. The end-point was by no means sharp, though a good approximation was probably obtained. The absorption of alkali corresponded to 2.0–2.2 ml. of *N* NaOH per g. of wood.

The results of the treatments, calculated as furfuraldehyde % of the original, dry, unextracted woods, are shown in Table 1. The standard deviation of the mean of quadruplicates is ± 1.06 % of that mean for mahogany, and ± 0.61 % of that mean for willow; the greater precision in the latter case is due to the greater homogeneity of the sample. The standard deviations of differences, (a)–(b) and (b)–(c), are calculated independently in each case from the standard deviations of the pair of quadruplicate means concerned.

It will be observed that the results of treatment (d) do not differ significantly from those of (b), though it may be more than coincidence that degradation

Table 1. *Furfuraldehyde as percentage of original wood*

	Control (a)	Residue + extract (b)	Residue + extract (d)	Residue (c)	Degradation loss (a) - (b)	Extract (b) - (c)
Mahogany	9.17	—	—	—	—	—
1 % NaOH, alcohol 10 %	—	8.53	—	7.62	0.64 ± 0.132	0.91 ± 0.121
30 %	—	8.70	—	7.99	0.47 ± 0.134	0.71 ± 0.125
50 %	—	8.70	—	8.42	0.47 ± 0.134	0.28 ± 0.128
70 %	—	8.60	—	8.61	0.57 ± 0.133	—
90 %	—	8.56	—	8.74	0.61 ± 0.133	—
Willow	14.55	—	—	—	—	—
1 % NaOH, alcohol 10 %	—	13.00	13.08	10.38	1.55 ± 0.119	2.62 ± 0.101
30 %	—	13.14	13.20	11.32	1.41 ± 0.120	1.82 ± 0.106
50 %	—	13.24	13.26	12.28	1.31 ± 0.120	0.92 ± 0.110
70 %	—	13.12	13.14	13.39	1.43 ± 0.120	—
90 %	—	13.04	13.19	13.08	1.51 ± 0.120	—

with (d) is represented by smaller values throughout than with (b). However, (d) need not be discussed further.

The similarity of behaviour of the two woods is very great. With both the degradations losses show little change with variations in alcohol concentration, though the loss with willow is relatively and absolutely greater than with mahogany. The extract behaviours are likewise similar, though willow yields a considerably greater amount of material soluble in 10, 30 and 50 % alcoholic-1 % NaOH. There is a slight irregularity in the results from the 70 and 90 % extracts, but the figures obtained for the difference (b) - (c) are not significant (with the possible exception of the 70 % willow extract) and this matter may at present be ignored. The extracts containing up to 50 % of alcohol have removed the equivalents of amounts of furfuraldehyde which diminish as the alcohol concentration increases, and it is apparent that the extraction of furfuraldehyde-yielding material has substantially stopped by the time the alcohol concentration reaches 70 %. The regular decrease in extraction appears to support the contention that we are not dealing here with any special type of hemicellulose.

Working with straws, Norman [1935] reported an apparently greater extraction of polyuronides with 30 % alcohol-1 % NaOH than with aq. 1 % NaOH. With willow, aq. 1 % NaOH gave an extract furfuraldehyde of 2.40 % with a degradation loss of 2.16 %. The degradation loss is significantly greater than in any of the alcohol treatments, and it is obviously extremely difficult to attempt comparison between the present results and those of Norman, which took no account of the destruction of furfuraldehyde. Comparison is rendered further inadvisable by the fact that crude straw was used, whilst the willow had undergone preliminary treatment which included extraction with alcohol. Balancing any repressive effect that alcohol may have on degradation, it has previously been shown [Preece, 1940] that material soluble in alcohol may protect furfuraldehyde-yielding material against destruction; it may well be that such alcohol-soluble material also impedes extraction of hemicelluloses, dissolution being then favoured by even low concentrations of alcohol in the extracting medium.

Qualitative extraction

The following general method of 'lignosaccharide' and hemicellulose preparation was applied to fresh samples of both sawdusts, 750 ml. of each extractant being used per 100 g. of wood. Extraction was carried out at boiling temperature for 1 hr. each with: (i), (ii) aq. ammonium oxalate solution; (iii) distilled water; (iv), (v) x % alcohol-1 % NaOH; (vi), (vii) x % alcohol. The wood

residue was dried in air and reserved; it is designated lr_x . The values of x used were 10, 30 and 50 %. Extracts (i), (ii), (iii) and (vii) were discarded, but (iv), (v) and (vi) were combined and filtered through pulp. The volume of N HCl necessary to adjust the whole to neutrality was determined by titration of an aliquot portion by the minimum conductance method. The neutralized extract was concentrated under reduced pressure to about 1/4 vol., further concentration not being attempted since there is reason to suppose that high salt concentrations may interfere with hemicellulose precipitation. An equal volume of acetone was added and the precipitate, l_x , was purified as described later. Precisely one-half of the residue lr_x was extracted for successive 2-hr. periods with (viii), (ix) and (x) aq. 4 % NaOH at room temperature; repeated washings with water were then applied, after which the residue— hr_x —was dried in air and reserved. Hemicelluloses— h_x —were precipitated from the combined and filtered NaOH extracts by acidifying with HCl and adding an equal volume of acetone.

A further hemicellulose preparation, h , was made by extracting the wood by methods (i), (ii) and (iii), the extracts being discarded. The residue was then treated as under (viii), (ix) and (x), the hemicellulose being precipitated from these three combined extracts. The washed and dried wood residue is designated hr .

A measure of purification of the mahogany preparations was obtained by dissolving or suspending them in 2 % NaOH and reprecipitating with acetone after acidifying with HCl. The willow preparations, on the other hand, were all passed through the Cu purification method, after filtration of their NaOH solutions. Analyses of the products are shown in Table 2.

Table 2. *Analysis of hemicelluloses*

Preparation	On dry, ash-free hemicellulose			Furfuraldehyde on dry, ash-free, lignin-free material %
	Yield, on dry wood %	Lignin %	Furfuraldehyde %	
Mahogany h	2.30	4.33	54.26	56.72
h_{10}	1.90	1.67	53.33	54.24
h_{30}	2.11	2.23	55.81	57.08
h_{50}	2.15	1.45	55.21	56.02
l_{10}	1.72	21.34	31.48	40.02
l_{30}	0.70	25.47	27.59	37.02
l_{50}	0.16	35.38	21.90	33.89
Willow h	10.64	1.06	57.53	58.15
h_{10}	5.61	0.79	57.34	57.79
h_{30}	7.00	0.98	57.82	58.39
h_{50}	8.92	0.85	56.26	56.74
l_{10}	3.07	7.22	48.12	51.92
l_{30}	1.38	6.03	49.41	52.58
l_{50}	0.22	11.90	37.63	42.71

Much of the lignin of the mahogany preparations of the l_x series has been carried down mechanically; thus, mahogany l_{10} was purified from a filtered NaOH solution by Cu treatment and then gave (on the ash-free basis): furfuraldehyde 38.09 %, lignin 5.13 %. Correcting the furfuraldehyde result for the lignin content the figure becomes 40.15 %; evidently the purification has not modified the composition of the lignin-free material, of which 82 % was recovered by the technique adopted. It is clear that alcohol and acetone washes alone cannot be relied on for removal of lignin. The alcoholic-NaOH pretreatment has markedly reduced the lignin content of mahogany preparations h_x as compared

with h ; with willow the corresponding differences are insignificant. It appears that, with both woods, the Cu-purified preparations l_x give markedly more lignin than the corresponding members of the h_x series. The variations in furfuraldehyde yield for h and h_x from a given wood are small and somewhat irregular; these furfuraldehyde yields always exceed those for l_x , even after correction for lignin. The yields of l_x show again the restricting effect of increasing alcohol concentration.

The wood residues

The seven residues from each wood, and the original woods themselves, were examined for furfuraldehyde yield and for their content of Cross and Bevan cellulose, the furfuraldehyde yield from this crude cellulose being also determined. No pretreatment was applied in the cellulose determination, except that the original wood samples were extracted with alcohol-benzene mixture. Chlorination was for periods of 20 and 15 min., followed by further treatments as required of 10 min. each. The results are shown in Table 3, where the compositions of the crude celluloses are also given, it being assumed that the furfuraldehyde is derived exclusively from xylan, pure cellulose (glucosan) being obtained by difference.

Table 3. *Analysis of wood residues*

	Wood	lr_{10}	lr_{30}	lr_{50}	hr_{10}	hr_{30}	hr_{50}	hr
Mahogany:								
On dry wood or residue, %:								
Total furfuraldehyde	9.30	9.88	9.95	10.01	8.22	8.19	8.38	8.20
Cross and Bevan furfuraldehyde	5.02	6.84	6.86	6.71	6.23	6.37	5.68	5.92
Chlorination loss	4.28	3.04	3.09	3.30	1.99	1.82	2.70	2.28
Cross and Bevan cellulose	53.64	63.92	62.63	61.34	65.30	67.75	65.01	62.55
On Cross and Bevan cellulose, %:								
Glucosan	85.5	83.4	83.0	83.0	85.2	85.4	86.4	85.3
Para-xylan	14.5	16.6	17.0	17.0	14.8	14.6	13.6	14.7
Willow:								
On dry wood or residue, %:								
Total furfuraldehyde	14.49	14.12	15.30	15.68	8.37	9.40	9.27	8.81
Cross and Bevan furfuraldehyde	9.73	12.43	12.88	13.00	7.54	8.13	7.89	7.17
Chlorination loss	4.76	1.69	2.42	2.68	0.83	1.27	1.38	1.64
Cross and Bevan cellulose	59.93	73.09	72.18	70.58	70.45	71.56	70.00	68.13
On Cross and Bevan cellulose, %:								
Glucosan	74.8	73.6	72.5	71.4	83.4	82.4	82.5	83.7
Para-xylan	25.2	26.4	27.5	28.6	16.6	17.6	17.5	16.3

The figures for Cross and Bevan cellulose on dry wood or residue indicate the relative efficiencies of extraction of cellulosic and non-cellulosic materials. Thus, with both woods, increasing concentration of alcohol in the alcoholic-NaOH pretreatments diminishes the proportionate extraction of non-cellulose, whilst with mahogany the subsequent extraction with 4% NaOH further enhances the cellulose content of the residue, this extractant having here removed proportionately more non-cellulose than cellulose. With willow, on the other hand, the result of 4% NaOH extraction after alcoholic-NaOH pretreatment is to diminish the cellulose content of the residue; clearly, in this case, cellulose has been extracted more effectively than non-cellulose.

Again, no matter what pretreatment or extraction has been applied, chlorination always removes more furfuraldehyde-yielding material from the residue. Two possible explanations suggest themselves; either the various NaOH treatments increase the susceptibility of the para-xylan to the effects of chlorination

and sulphite extraction, or these NaOH treatments fail to remove the whole of the encrusting hemicelluloses. Whilst the first alternative is not to be overlooked, there is direct evidence to support the second; thus, Preece [1931] has shown that hot alkaline extraction of wood residues may continue to remove urono-pentosan after exhaustive extraction in the cold has failed to take any further appreciable amount into solution.

The variations found in the compositions of the various Cross and Bevan celluloses are of the first importance, and it may be remarked that a difference in para-xylan content exceeding 0.5 % between two samples may be considered significant. With mahogany, the compositions of the celluloses from the original wood and from the residues hr , hr_{10} and hr_{30} are substantially identical. Clearly this result by itself is most misleading; it must simply be implied that xylan and glucosan have been proportionately removed. It is apparent that, with this wood (and with willow also), hot alcoholic-NaOH removes glucosan more effectively than xylan, whilst with cold 4 % NaOH the reverse is true. Thus, the observed cellulose compositions depend only on the differing rates of extraction of the components; there is every reason to believe that both components are removed to greater or less extents by the various NaOH treatments applied. These results, especially in so far as they relate to hot alkaline extraction, may be compared with those recently obtained by Mackney [1940].

DISCUSSION

The figures of Table 1 amply confirm the destructive effect of boiling alcoholic-NaOH on furfuraldehyde-yielding substances, and it is interesting to note that the magnitude of the loss, while but little affected for a given wood by the alcohol concentration, does vary considerably with different woods. Thus, for 50 % alcohol-1 % NaOH the losses for teak, mahogany and willow are respectively 4.2 % [Preece, 1940], 5.1 % and 9.0 % of the total furfuraldehyde, these being the figures when a pretreatment including alcohol extraction had been given. It appears that there may be a further source of loss. In Table 4

Table 4. *Hemicellulose yields*

Preparation	From mahogany		From willow	
	Calc. %	Actual %	Calc. %	Actual %
l_{10}	2.89	1.72	5.44	3.07
l_{30}	2.58	0.70	3.68	1.38
l_{50}	1.27	0.16	2.44	0.22

are given the calculated (Tables 1 and 2) and actual (Table 2) yields of hemicellulose soluble in alcoholic-NaOH. The yields obtained fall very short of those calculated and it is probable that depolymerization of some of the hemicellulosic material renders it incapable of precipitation by the usual means. More direct evidence of loss of hemicellulose is provided by noting that direct extraction of willow with 4 % NaOH gave a 10.64 % yield of hemicellulose; in no case with this wood did the combined yields of l_x and h_x approach this figure. On the other hand, the direct yield from mahogany is exceeded by $(l_{10} + h_{10})$ and by $(l_{30} + h_{30})$. There can be no doubt that the alcoholic-NaOH treatments do cause the dissolution of more hemicellulose than would be the case with direct cold extraction alone, but whether this increased dissolution is reflected in the yields obtained depends entirely on the susceptibility to degradation of the material concerned.

The evidence is complete that hemicelluloses without exception contain material (cellulosan) which is resistant to chlorination and also material (encrusting hemicelluloses) which is removed by this treatment. Indeed, in the case at least of the willow preparations, the amount of cellulosan present probably predominates. Table 3 indicates that the residues of the lr_x series yield more crude cellulose than the corresponding members of the series hr_x . This can only be the case if cellulosic material is removed more completely than non-cellulose (including encrusting hemicelluloses) by the intervening NaOH extraction. In fact, with the figures given, the cellulosan passing into the hemicellulose extract must exceed twice the amount of non-cellulosan, not all of which need be encrusting hemicellulose. Certainly, however, the differences between willow pairs are not significant except in the case of lr_{10} and hr_{10} ; nevertheless, this scarcely affects the above argument. The influence of direct cold extraction with 4% NaOH on furfuraldehyde-yielding cellulosan materials is shown by a comparison of the para-xylan figures for the cellulose of willow wood and that of the residue hr (Table 3).

Hot extraction likewise gives mixtures of hemicelluloses, but the tendency here is towards increased removal of non-pentosan. The relatively low figures for 'lignosaccharide' furfuraldehyde thus appear to be largely accounted for by relatively high glucosan contents, though there may also be differences in uronic anhydride, a point which has not here been investigated. 'Lignosaccharide', therefore, does not differ from hemicelluloses extracted in the cold, except in the proportions of the various components of the mixture. It may be noted that hot extraction, which favours the dissolution of glucosan, also gives fractions showing higher lignin figures when examined by the Schwalbe method; a difference persists even when careful Cu purification is applied. It is possibly worthy of investigation whether these fractions contain high proportions of material either (i) chemically associated with lignin or (ii) of such modified properties as to give products resistant to 72% H_2SO_4 -18% HCl treatment.

It is abundantly clear therefore that the methods of hemicellulose preparation at present employed give mixed products. It has been claimed on various occasions to separate preparations into fractions that were 'chemically and physically distinct' [Norris & Preece, 1930]; exception has been taken to such claims, but it has never been implied that the fractions were homogeneous. Again, Preece [1931] showed that the analysis of box-wood hemicellulose could be interpreted as indicating a relatively simple composition; but here again there was no suggestion that a simple 'pure' product was, in fact, concerned. The dangers of the problem are further indicated by comparing the results for maize-cob hemicelluloses obtained by Preece [1930] with those for the same materials of Angell & Norris [1936]. The latter authors show that, by careful control of pH, Preece's fractions A_1 , B_1 and C_1 can be precipitated as a single fraction. However, A_1 , B_1 and C_1 show distinct differences in chemical composition, even though the partial separation achieved may have been fortuitous; evidence of the possibility of even a partial fractionation would appear to be more informative than the demonstration that, under other conditions, separation is avoided. Further, in relation to these maize-cob products, it now seems certain that their chemical analysis is to be accounted for on the assumption that the products of hydrolysis are pentose, uronic acid and glucose.

SUMMARY

1. Loss of hemicellulose material as a result of boiling alkaline pretreatment is confirmed.
2. Hot alkaline extraction of woods favours the dissolution of non-pentosan; extraction in the cold favours the dissolution of xylan.
3. Hemicellulose preparations contain materials derived both from the encrusting hemicelluloses and from the cellulose fraction; the relative proportions of the components of the mixture vary with the conditions of extraction and with the raw material.
4. The mixed nature of hemicellulose preparations is stressed.

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