CCXC. THE ASSOCIATION OF XYLAN WITH CELLULOSE IN CERTAIN STRUCTURAL CELLULOSES.

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THE cellulose of most plant materials and woods differs from cotton cellulose in many respects. In the first place, separation from other cell wall constituents can only be achieved by a more or less severe treatment, in contrast to that of the cotton hair which can readily be purified. In the second place, the product obtained, while consisting mainly of "true cellulose" as typified by that of cotton, is not exclusively so, and contains also other polysaccharides, intimately associated and tenaciously retained. For this group Hawley & Norman [1932] have suggested the name "cellulosan" implying thereby a hexosan or pentosan found with the cellulose and held in some way by it. In this paper will be described some observations on the celluloses of certain plants, mostly cereal straws, which have a high cellulosan content. Attempts have been made by chemical means to obtain information as to the relationship between the "true" cellulose and associated cellulosans. A parallel investigation, involving the X-ray examination of cellulose fibres high in cellulosan, has been carried out in conjunction with Mr W. T. Astbury and will be reported later.

The present concept of the structure of the cellulose molecule has been developed by a combination of chemical and physical methods, which have shown that the peculiar and valuable properties of cellulose are not conferred by its molecular size so much as by the state of molecular aggregation in which it ordinarily exists. While actual replacement of any of the side hydroxyls in the units of the cellulose chain would not affect the strength of the chain longitudinally, the increased separation of the chains by the substitution of larger groups for the hydroxyls would tend to weaken the fibrous structure of the aggregate by overcoming the secondary valency forces responsible for lateral stability. It is stated that nitrocellulose retains its fibrous structure better than the acetate, since in the latter wider separation is brought about. In view of these facts, the existence of lignocellulose or pectocellulose as a definite combination between oriented cellulose and lignin or pectin cannot be admitted and the possibility of direct combination between cellulose and cellulosans is similarly ruled out. The evidence to be presented is in accord with the view that the cellulosan molecules participate in the cellulose micellae and crystallites in the same way as do the individual cellulose chains. The commonest cellulosan is xylan, though in *Gymnosperms* mannan is characteristic. The xylan from *esparto* has been shown to be a 1:4-anhydroxylose, the xylose units being of the normal amylen oxide type [Hampton *et al.*, 1929]. A terminal group of *l*-arabinose has also been detected in this particular case [Haworth *et al.* 1934]. The xylan unit therefore differs from the glucose unit in cellulose only in that the terminal carbinol group is missing. Such units are of the same size and would occupy the same space

longitudinally. The mannan formed in the cellulose from Gymnosperms has not been investigated, but by analogy is likely to be also a 1:4-anhydrohexose and, therefore, sterically similar in size to the cellulose and xylan with which it is so intimately associated.

The cellulosans are probably laid down with the cellulose as it is formed and participate in the oriented bundles of molecules that form the micellae of the fibres. They would be retained by secondary valency forces just as the cellulose chains are themselves stabilized in that way. Because of the absence of a projecting carbinol group, in the case of xylan at least, these forces might be expected to be less powerful than those between the cellulose molecules themselves. Some evidence will be presented later on the relative rates of removal of xylan and mannan from natural celluloses containing both. Further, the molecular size, or rather the length of the chain of sugar units, is considerably less in the case of the cellulosans than in cellulose itself. As a result of their retention by secondary valencies weaker than those between the cellulose chains and of their smaller molecular size they might be expected to be extractable, if with some difficulty. The actual form of participation of the cellulosans in the micellae is, at present, a matter of speculation. They undoubtedly form a normal integral part of the cellulosic structure of the plant cell wall and fibres, and any study of natural celluloses should include this group in as unchanged a condition as possible.

PREPARATION OF CELLULOSE.

Norman & Jenkins [1933] described a method for the determination of cellulose which could readily be adapted for large-scale preparations. Previously chlorinations for the removal of lignin have been carried out by some modification of the original procedure of Cross & Bevan [1918] employing gaseous chlorine, by which means it is impossible on a laboratory scale to treat more than a few g. at a time. By the use of dilute hypochlorite solutions quantities up to 1 kg. may be readily treated. Six or seven treatments are required for such materials as cereal straws in bulk and rather more for woods. The final washing must be continued until no trace of sulphite is detectable in the filtrate.

A. EFFECT OF HEAT ON CELLULOSE PREPARATIONS.

Cellulose preparations containing cellulosan undergo an irreversible change on oven-drying, as a result of which a fraction becomes soluble in hot water. If this be removed and the preparation again oven-dried, a further but smaller fraction can be extracted. This process can be repeated apparently indefinitely. Fig. 1 shows the losses from a sample of oven-dried wheat straw cellulose on boiling with water, the cellulose being oven-dried overnight between each

Table I. *Extraction of wheat straw cellulose, wet and oven-dried.*

Treatment		Total loss %		Loss of xylan %	
		Wet	Dry	Wet	Dry
3.0 %	Na ₂ SO ₃ 2 × 20 min. hot	5.0	7.6	1.1	2.8
0.25 %	NaOH 1 hour hot	11.7	19.0	3.3	6.0
1.0 %	NaOH 1 hour hot	17.5	22.0	5.4	7.2
4.0 %	NaOH 3 hours cold	18.8	22.5	13.2	16.4
0.25 %	H ₂ SO ₄ 1 hour hot	9.4	11.7	4.7	6.2
2.5 %	H ₂ SO ₄ 1 hour hot	11.9	15.6	7.7	10.4

Initial furfuraldehyde yield 13.88 %, equivalent to 21.59 % xylan.

treatment. After the fifth extraction the xylan content of the residue was determined. Whereas the aggregate loss was 18.8% the xylan removed accounted for only 8.9%, or about half.

The effect, therefore, is not solely concerned with the cellulosan fraction. Further, the effect of heat-drying also renders the cellulose preparations more susceptible to extracting and hydrolysing agents, as shown in Table I in which the losses from wet and dried preparations are compared. Again, the differences are not wholly due to an effect on the xylan, and must arise in part from a change in properties of a portion of the "true" cellulose fraction.

To determine whether this effect is due to the removal of water in drying or the application of heat, or both, a large batch of oat straw cellulose was subdivided and dried in different ways. These samples were then extracted by

Fig. 1. Water-soluble material produced on repeated drying of wheat straw cellulose (xylan 20.3%).

Fig. 2. Repeated extraction and drying of oat straw celluloses.

boiling with water for 15 min., and since the effect of certain initial treatments was noticed to persist after the first extraction, all the residues after drying for 16 hours at 100° were twice re-extracted with water and again dried. The results are summarized in Table II.

Exposure to heat seems to be the vital factor in this phenomenon. Whereas there was little difference in the material when air-dried, alcohol-dried or dried at 40°, higher temperatures enhanced the amount of water-soluble material obtainable. Air-dried or alcohol-dried samples subsequently exposed to heat were similar in properties to those directly given the same heat treatment when wet. Wet samples which were alternately rapidly frozen and thawed showed no change in properties.

Results of a similar character were obtained when extracting agents other than water, such as dilute acids and alkalis were employed. The effect of exposure to heat results in some modification of the properties of a portion of both components of isolated plant celluloses, which is manifest in increased susceptibility to extracting and hydrolysing agents. Moreover, this effect may be demonstrated repeatedly upon the same sample. The increments of water-soluble material become smaller, but are still appreciable after many treatments. In Fig. 2 the amounts removed from two samples of cellulose alternately dried and extracted are shown. Over the first twelve treatments the xylan

Table II. *Loss on water extraction of oat straw cellulose dried by various means.*

All results expressed on basis of 100 g. oven-dried material.

Series	Treatment of cellulose	Total loss		
		Extraction I	Residue from I, dried 16 hr. at 100° Extraction II	Residue from II, dried 16 hr. at 100° Extraction III
A	Wet	4.3	6.2	8.7
B	Air-dried; room temperature (moisture content 7.53%)	4.7	6.5	9.0
C	Alcohol-dried, room temperature	5.2	7.5	9.1
D	Dried at 40°	5.3	7.9	9.9
E	Dried at 60°	6.3	9.0	11.6
F	Alcohol-dried; put in benzene, heated under vacuum at 80° for 10 hr.	6.2	7.6	9.5
G	Dried at 80°	6.6	9.3	11.3
H	Oven-dried, 100° for 8 hr.	6.8	11.6	13.6
I	Air-dried, then heated at 100° for 16 hr.	7.6	9.7	14.0
J	Alcohol-dried, then heated at 100° for 16 hr.	7.1	10.9	14.2
K	Vacuum-dried, at 100°	8.1	10.2	12.8
L	Dried at 120° for 16 hr.	8.9	11.9	13.3
M	Dried at 150° for 16 hr.	9.6	11.7	14.2

Cellulose contained initially 32.3 % xylan.

removed accounted for about half the total loss and rather less after 20 treatments, at which point 80 % of the xylan had been removed, as compared with a loss of about 25 % of the "true cellulose". The xylan or cellulosan is therefore much the more susceptible fraction. Concurrently a distinct change in physical properties was observed on repeated extraction, the cellulose residue becoming less cohesive and losing the slightly gelatinous property which caused it originally to dry to a close hard mass, being instead light and friable.

Whilst the effect of heat on plant celluloses is to cause the formation of some water-soluble material, and whilst this effect can be repeated apparently indefinitely, it must be pointed out that pure cotton cellulose does exhibit the same phenomenon, but to a much smaller extent. An unbleached cotton yarn from

Table III. *Loss on water and citric acid extraction of cotton cellulose, oat and wheat straw cellulose after drying at 100° overnight.*

Expressed on 100 g. cellulose (oven-dried basis).

Extraction	Water: 15 min.			0.5% citric acid: 1 hr.		
	Cotton	Oat straw	Wheat straw	Cotton	Oat straw	Wheat straw
I	3.6	6.8	7.3	7.6	13.6	11.8
II	4.3	11.6	9.4	7.8	21.2	17.6
III	4.9	13.6	11.0	8.4	26.6	23.3
IV	5.2	17.1	13.0	8.7	28.8	25.1

high quality long fibre Egyptian cotton was treated with water and 0.5 % citric acid for comparison with cereal straw celluloses. The results are given in Table III.

The isolated celluloses of cereal straws, containing as they do some 20 % xylan, are clearly much more affected by heat-drying than is pure cotton cellulose entirely free from xylan. Since it is evident that the water-soluble material formed cannot be solely accounted for from the xylan, the inference is that the presence of cellulosan weakens the whole cellulosic aggregate and causes a greater degree of susceptibility to the effect of heat.

The nature of the water-soluble material.

The aqueous extract obtained on boiling an oven-dried cellulose preparation is only slightly reducing. For example, 1 g. oat straw cellulose extracted after oven-drying lost 68 mg. The extract titrated by the Shaffer-Somogyi [1933] micro-method contained reducing groups equivalent to 0.4 mg. glucose, a reducing value of 0.58 % on the material extracted. Having established that the water-soluble material produced by drying is not hydrolysed by aqueous extraction, preparations were made from various isolated celluloses. The dried cellulose was boiled with water for 15 min. and the extract, after filtration, concentrated to a small volume under reduced pressure. To this straw-coloured liquid 5 vol. of alcohol were added, the white precipitate which formed being washed with acid alcohol, dried with increasing concentrations of alcohol and finally in a desiccator over fused zinc chloride. The preparations were slightly greyish white in colour, very light and hygroscopic.

Analyses showed that the preparations contained both hexose and pentose units as would be expected and some uronic acid groups. The anhydropentose content varied from 60 to 75 % and uronic acid anhydride from 5 to 8 % according to the source. Acidic groups were titratable with *N*/50 NaOH using thymol blue as indicator. A study was made of the rate of hydrolysis of certain of these preparations, the reducing sugar formed being titrated by the Shaffer-Somogyi micro-method, with the modification that the time of heating was increased to 25 min. since the shorter period recommended for glucose did not give complete recovery of xylose. The initial reducing values before hydrolysis were low, but rather variable, from 0.17 to 3 % calculated as glucose. Hydrolysis by boiling with dilute mineral acids was rapid, but the recoveries of sugar were not very satisfactory. The shape of the hydrolysis curves did not suggest that there was a resistant portion unattacked by any of the acid strengths employed, but rather that the incompleteness of the recovery must be ascribed to destruction of sugar. It is known that high yields of xylose from xylan are difficult to obtain [Heuser & Brunner, 1922; Heuser & Jayme, 1923] and that the decomposition of pentoses during the hydrolysis of pentosans is greater than in controls of pure sugar similarly heated with acids. Since all the preparations were relatively rich in xylan, destruction of xylose probably accounted for the low sugar yields. The recovery of sugar from two preparations from oat straw cellulose is shown in Table IV.

Since a strong probability existed that these preparations were not homogeneous, an attempt was made at separation by precipitation at different alcohol concentrations. Four fractions, A, B, C, D, were obtained at 48, 65, 85 and 95 % alcohol concentrations respectively. The yields from 90 g. oat straw cellulose were A, 1.6 g.; B, 0.39 g.; C, 0.14 g. and D, 0.04 g. The furfuraldehyde yields indicated the xylan contents to be respectively 70.5, 43.4 and 52.8 %, the amount of D available being too small for any determination. The initial

Table IV. *Hydrolysis of water-soluble material from oven-dried oat straw cellulose.*

% sugar liberated expressed as apparent glucose.			
Acid concentration	Time	Prep. 1	Prep. 2
		Xylan content 68.5 %	Xylan content 73.4 %
5% H_2SO_4	5 hr.	88.3	89.2
2.5% H_2SO_4	3 hr.	82.9	89.8
1% H_2SO_4	3 hr.	82.8	86.5
10% oxalic	3 hr.	93.1	85.9
2.5% H_2SO_4	1 hr. at 1 atmos.	84.2	85.6
72% H_2SO_4	2 hr. cold, diluted to 3% and boiled 2 hr.	79.7	81.5
3% HNO_3	1 hr.	70.7	—

reducing value of the main fraction A was 1.09 % in terms of glucose. The hydrolysis curves obtained with 10 % oxalic acid and 0.15 N H_2SO_4 were similar in shape, and the recoveries of sugar again unsatisfactory.

Evidence that the main fraction A obtained at the lowest alcohol concentration was still not homogeneous was given by separation by other means. A small amount was dissolved in cold 1 % NaOH and Fehling's solution added. The blue precipitate which formed, after washing with 50 % alcohol, was suspended in alcohol containing HCl and washed free from copper. This precipitate was found to yield furfuraldehyde equivalent to a xylan content of 86 %. The yield however was small and did not represent all the xylan in the sample taken. A similar partial separation of xylan was effected by adding alcohol to the alkaline filtrate from the copper precipitation above. A fraction was obtained at an alcohol concentration of 50 % which on subsequent washing and drying was found to contain 84 % xylan. Both procedures gave a fraction richer in xylan than the original preparation, which might be held to substantiate the view that the hexosan and pentosan are not combined.

The alcoholic filtrates from the precipitation of the water-soluble substance contained a small quantity of material not precipitated even at an alcohol concentration of more than 95 %. This was obtained by distillation under reduced pressure to a very small volume which was then made up to 10 ml. The solution was golden brown in colour and strongly reducing. On hydrolysis with acid the reducing value increased only about four or five times, an indication that the molecular size of this fraction must have been small. Figures for three such residues are given in Table V.

Table V. *Reducing power of alcohol-soluble fraction.*

	Expressed as mg. glucose.		
	I	II	III
Direct	48.3	37.5	33.0
Hydrolysed for 1 hr. with 5% H_2SO_4	180.0	111.0	—
Hydrolysed for 3 hr. with 2.5% H_2SO_4	—	—	142.0

Changes in the cellulose as a result of drying.

There are few tests that can be applied to cellulose itself to obtain information bearing on the effect of heat-drying. Degradative changes are usually accompanied by an increase in the copper number as a result of the production of

reducing groups. Such an increase was observed, the method employed being the Heyes [1928] modification of the Schwalbe-Braidy procedure. A small concurrent increase was found in the yield of CO_2 on distillation with 12 % HCl presumably owing to the production of uronic acid groups. It is not certain, however, that all the CO_2 given by cellulose is due to this grouping. The figures are given in Table VI.

Table VI. *Changes in copper number and CO_2 yield on drying wheat cellulose.*

Treatment of cellulose	Copper number*	CO_2 number†
Wet	0.60	0.30
Air-dried	0.75	0.43
Oven-dried, 16 hr.	0.83	0.45
Oven-dried and extracted with water twice, then air-dried	0.98	0.46
Oven-dried, 48 hr.	2.07	—

* Weight of copper reduced by 100 g. cellulose (dry).

† Yield of CO_2 on distillation of 100 g. cellulose (dry).

The changes, though small, are in the same direction as observed in the production of oxycelluloses and are, no doubt, of a similar type.

Discussion of the above observations.

This effect of heat drying of plant celluloses does not appear to have been directly recorded before, though in a brief paper by Sherrard & Blanco [1932] some experiments are given in which the same phenomenon undoubtedly occurred. They showed that from white spruce cellulose, kept wet, some material could be removed by prolonged boiling with water, but after drying the losses from the cellulose were heavier. Partial hydrolysis due to the long period of boiling was however the chief factor concerned in their experiments. From the extract, by concentration and precipitation with alcohol, a white powder was obtained, rather similar to those prepared in this work, in that it was very hygroscopic and easily hydrolysable to sugars. Experiments on the drying of wood made by Campbell & Booth [1930; 1931] showed a slight increase in the hot water-soluble fraction as a result of treatment at 100° or 105° , a fall in the Cross & Bevan cellulose content and a definite increase in alkali-solubility. These changes may be in part accounted for by the effect of heat on the cellulosic fraction.

The observations described in this paper do not admit of any ready explanation on the basis of present theories of the arrangement of cellulose molecules. The removal of water by drying is likely to modify conditions within the micellae. Shrinkage will occur and strains be set up as a result of the withdrawal of the "packing" provided by the water molecules. This disturbance might be expected to make for an increased susceptibility to the hydrolytic action of boiling water or stronger reagents. The observed effect of heat is, however, more difficult to understand. Alcohol-dried and air-dried samples subsequently exposed to a temperature of 100° were considerably affected by this further treatment from which water relationships are excluded. The effect of moderate temperatures on cellulose has been little studied. Profound changes take place on prolonged heating; indeed, it has been stated that complete carbonisation may occur in the course of a few months at 120° . Knecht [1920] has shown a rapid loss of colour and strength in cotton exposed at 93° . Whatever be the nature of the changes caused by the application of heat, plant celluloses containing cellulosesans are very much more affected than is pure cotton cellulose. Both the initial loss on extraction and the further increments obtained by repeating the treatment are

considerably larger than in the case of cotton. The extra amounts are only in part accounted for by the cellulosan removed. The "true" cellulose aggregate is therefore less resistant than cotton or is weakened in this respect by the presence of cellulosan molecules within the micellae. The preparations of water-soluble material obtained do not throw much light on the nature of the changes responsible for the production of this fraction. The presence of two components which are undoubtedly affected to a different extent by the treatments means that any preparation will be a mixture. The cellulosan fraction is more affected by heat treatment than is the "true" cellulose since the xylan content of the water-soluble preparations was about 70 %. It must be presumed that the effect of heat is to cause a breakage of some of the cellulose chains, and probably but not essentially a breakage of the xylan too. Evidence for chain breakage is provided by the increase in "copper number" values.

At the same time, some oxidation undoubtedly occurs with the production of uronic groupings and possibly also of terminal carboxyl groups of the gluconic type which would not be included in the estimation by CO_2 yield. Without assuming definite breakage of the cellulosic chains as a result of heat, it is not possible to account for the production of further water-soluble fractions, apparently similar, on wetting and re-exposing to heat. The water-soluble material may be supposed to consist of cellulosic fragments still of considerable though variable size and partially oxidized, mixed with cellulosan or degraded cellulosan molecules. Fractionation of the water extract was undertaken since it seemed likely that cellulosic fragments of diminishing molecular size might be precipitated by increasing alcohol concentrations and that differences in these might be evident in the rates of hydrolysis. In fact, however, the major part of the material removed precipitated at a relatively low alcohol concentration. No information exists as to the limit in number of glucose units in a chain imposed by water-solubility. A very small portion of the extract was strongly reducing and, since hydrolysis increased the reducing value only three or four times, the chain length of this fraction was probably quite short. The reducing value of the preparations was low, but cannot be taken as a reliable or even approximate index of average chain length because, owing to oxidation, the terminal groups might well be carboxylic rather than aldehydic in nature.

These observations may be of practical importance in two directions. In the first place, there is the possibility that the drying of any plant material before isolation or determination of the cellulose in it may have so changed the balance between cellulose and cellulosan that the product obtained is not truly representative. It is not certain that *in situ* and in association with other cell wall constituents such a change would occur. If it does, this is clearly a normal process in senescence and would take place during the ripening of straw, for example. Experiments to test this point are at present inconclusive, owing to the difficulty of grinding fresh tissues to as fine a state of division as dried materials. In routine work, at present, cellulose determinations are carried out on air-dried rather than oven-dried material.

A further implication of this work lies in the decomposition of cellulose by micro-organisms. The fermentation of celluloses which contain cellulosan has been little studied, the substrate in most work of this type being the pure celluloses of filter-paper or cotton. Heat treatment of a plant cellulose by producing a water-soluble fraction might expedite attack on the aggregate. If higher temperatures, possibly up to 140° , were employed, such a preliminary "cracking" might result in a more effective and rapid decomposition. This point is at present under investigation.

B. HYDROLYSIS AND EXTRACTION OF CELLULOSE PREPARATIONS.

Although most celluloses consist of two components, cellulosan and "true" cellulose, no quantitative separation has ever been achieved. The properties of the cellulosans are, with certain limitations, those usually described for the encrusting polyuronide hemicelluloses. That is to say, they are soluble in cold dilute alkalis and hydrolysed to their constituent sugars by boiling with dilute mineral acids. Limitations are conferred by reason of their association with the cellulose. The purpose of the work to be described was to investigate the removal of the cellulosan fraction of some celluloses by hydrolysis with acids and extraction with alkali.

There are few references in the literature to any previous work on this subject, indeed, only one paper, by Hawley & Fleck [1927], deals directly with the action of dilute acids on isolated cellulose. They showed that wood cellulose is hydrolysed much more readily than cotton cellulose and claimed that from softwood cellulose all the mannan and most of the pentosan might be removed with ease. The effect of dilute acids on cotton cellulose, as followed by the liberation of sugar, was determined by Wohl & Blumrich [1921] who found that the acid extract filtered free of cellulose had an increased reducing value on further boiling, indicating the presence of some compound intermediate between cellulose and glucose. A number of workers have studied the hydrolysis of wood with dilute mineral acids at ordinary temperatures and under pressure. Miller & Swanson [1925] showed that as a result of such treatment the cellulose is much reduced, a portion being lost at very low acid concentrations. This easily hydrolysable portion, amounting to about 13 % of the cellulose, was, no doubt, largely cellulosan in nature.

Only recently has it been realized that the cellulose of plant materials and woods is much less resistant to the action of acid and alkali than is cotton cellulose. Any treatment other than in neutral solution should be avoided in handling materials from which the cellulose is to be prepared or determined, in order that the integrity of the cellulose may be preserved. The nature of the attack brought about by acid and by alkali is shown in the following experiments. In view of the observations on the effect of heat-drying, all preparations were kept wet, and the treatments to be described were carried out on the wet material, due allowance being made for the moisture content.

1. *Hydrolysis.*

The effects of hydrolysis were studied by treating small samples for various times under standard conditions. The residues after thorough washing and drying were weighed and used for furfuraldehyde determinations. Reducing sugars were estimated directly in the extract using the Shaffer-Somogyi [1933] micro-method. The acid extract was also further hydrolysed by boiling again for 3 hours after adjusting the acid concentration to 4 % in each case. The reducing values of the extract both direct and after rehydrolysis are expressed as apparent glucose, it having been determined that the curve for xylose with this reagent is almost identical with that for glucose. With this information a full picture of the changes taking place on hydrolysis may be obtained. In Tables VII and VIII respectively are given the results obtained on the celluloses of oat straw and oak.

Considering first the series on oat straw cellulose given in Table VII, this cellulose was found to undergo appreciable loss with acid as dilute as 0.1 % ($N/50$) and in a period as brief as half an hour. Hydrolysis was progressive with time in this and all higher concentrations. Three important facts emerge and may

Table VII. *Hydrolysis of oat straw cellulose with acids at the boiling point.*
Furfuraldehyde yield = 17.82% equivalent to xylan 27.62%.

All results expressed on the basis of 100 g. original cellulose.

Conc. of H ₂ SO ₄ %	Time in hr.	Residue	Xylan in residue	Xylan lost	Hexosan lost (diff.)	Sugars in extract	Sugars on re- hydrol.	Xylan loss Total loss %
0.1	$\frac{1}{2}$	93.1	23.4	4.2	2.7	2.7	8.8	61
	2	89.3	21.4	6.3	4.4	4.2	10.2	59
	5	88.2	20.8	6.8	4.9	6.0	12.1	58
	16	84.4	17.1	10.5	5.0	10.7	13.7	67
0.25	1	87.3	19.8	7.8	4.8	4.5	9.9	67
	2	85.7	18.1	9.6	4.8	6.5	12.2	67
	3	84.6	17.5	10.1	5.3	7.4	12.5	66
	5	82.7	16.2	11.4	5.8	10.5	13.1	66
	16	79.4	15.0	12.6	8.0	14.8	14.2	66
1.0	$\frac{1}{2}$	85.6	17.1	10.5	3.9	5.8	11.7	73
	1	83.9	16.9	10.7	5.3	8.6	13.9	67
	2	82.8	16.3	11.3	5.9	12.0	14.6	66
	3	81.7	15.2	12.4	5.9	13.5	14.8	68
	5	81.3	14.1	13.5	5.2	15.9	16.9	72
	16	77.2	8.9	18.7	4.1	22.4	21.4	82
3.0	$\frac{1}{2}$	84.7	16.8	10.8	4.5	10.9	14.4	71
	1	82.8	15.2	12.4	4.7	14.2	15.8	72
	2	80.7	12.8	14.8	4.5	17.1	17.7	77
	3	79.1	11.5	16.1	4.8	18.0	18.9	77
	5	76.5	9.9	17.8	5.7	19.4	20.3	76
	16	72.0	5.6	22.0	6.0	24.9	25.5	79
5.0	$\frac{1}{2}$	81.6	14.4	13.2	5.1	13.3	15.4	72
	1	80.6	13.8	13.9	5.6	16.5	16.9	72
	2	78.1	11.7	16.0	5.9	19.2	20.3	73
	3	76.2	9.9	17.7	6.0	21.2	—*	75
	5	74.7	8.1	19.5	5.8	24.0	—*	77
	16	67.3	3.5	24.2	8.6	27.3	—*	74

* Not determined.

be enumerated at once. Firstly, there is no apparent break in the continuity of the reaction with any of the concentrations of acid employed. If the effect produced on the cellulose in any selected time is plotted against the acid concentrations smooth curves are obtained, giving no indication of a fraction or fractions particularly susceptible to removal. Secondly, in no case did the xylan removed account for the whole of the loss sustained by the cellulose. There was evidently a concurrent extraction of hexosan, which presumably has to be considered as an attack on the true cellulose, though this point will be discussed more fully later. Thirdly, the reducing values of the filtered extracts obtained with all the lower acid concentrations were such as to indicate that the material removed had not undergone complete hydrolysis to reducing sugars. On increasing the acid concentration of the filtered extract to 4% in those cases in which it was originally less than this, on further boiling, the reducing values increased until the apparent sugar content was approximately equivalent to the total loss in the natural cellulose. The agreements were not very precise, no doubt owing to the instability of xylose in dilute mineral acid as referred to in the previous section.

Reviewing the series as a whole, the xylan may be said to be fairly readily removable by dilute acids, the maximum loss of 87% of the total xylan being achieved in 16 hours with 5% acid. With lower concentrations and in shorter periods the amount was almost proportionately less. The same, however, is not

Table VIII. *Hydrolysis of oak cellulose with acids. Furfuraldehyde yield = 15.93% equivalent to xylan 24.69%. Lignin = 0.79%.*

All results expressed on the basis of 100 g. original cellulose.

Conc. of H ₂ SO ₄ %	Time in hr.	Residue	Xylan in residue	Xylan lost	Hexosan lost (diff.)	Sugars in extract	Sugars on re- hydrol.	Xylan loss Total loss %
0.1	$\frac{1}{2}$	92.3	20.2	4.5	3.1	0.5	1.9	59
	1	90.1	19.8	4.9	4.9	0.9	5.1	50
	2	88.5	18.8	5.9	5.6	1.7	6.8	51
	3	88.0	18.0	6.7	5.3	2.3	7.4	55
	5	86.1	17.7	7.0	6.8	3.6	8.4	50
	16	83.9	16.0	8.6	7.5	8.5	11.2	53
0.25	$\frac{1}{2}$	90.3	20.1	4.6	5.1	1.0	5.1	48
	1	89.7	19.1	5.6	4.7	2.0	6.5	54
	2	87.8	17.9	6.7	5.4	3.5	8.3	55
	3	86.1	17.6	7.0	6.8	5.8	9.9	50
	5	85.4	17.3	7.4	7.2	8.0	10.5	51
	16	81.1	12.9	11.8	7.1	12.9	11.6	59
1.0	$\frac{1}{2}$	88.1	17.5	7.2	4.7	3.0	7.8	61
	1	87.2	17.3	7.4	5.4	5.9	8.9	58
	2	84.9	16.1	8.6	6.6	9.1	11.7	57
	3	83.7	15.4	9.3	7.0	11.1	13.1	57
	5	80.8	13.4	11.3	7.9	14.9	15.2	59
	16	74.2	8.8	15.9	9.9	19.3	—*	62
3.0	$\frac{1}{2}$	86.7	16.4	8.3	5.0	7.9	10.6	62
	1	84.4	15.0	9.6	6.0	12.1	12.4	62
	2	81.1	13.0	11.7	7.2	15.1	16.3	62
	3	77.8	10.9	13.8	8.4	16.4	16.4	62
	5	74.7	8.5	16.2	9.1	20.2	—*	64
	16	69.3	4.2	20.5	10.2	24.6	—	67
5.0	$\frac{1}{2}$	84.5	14.8	9.8	5.7	11.2	11.0	63
	1	79.9	12.5	12.2	7.8	15.5	16.2	61
	2	76.9	10.1	14.6	8.5	18.4	18.3	63
	3	75.4	8.9	15.8	8.8	22.1	—*	64
	5	71.3	6.4	18.3	10.4	23.5	—	64
	16	64.9	2.8	21.9	13.2	25.5	—	62
10	$\frac{1}{2}$	76.2	9.9	14.8	9.0	10.8	—	62
	1	73.6	8.6	16.1	10.3	13.1	—	61
	2	68.8	5.8	18.8	12.4	15.0	—	60
	3	66.8	4.4	20.3	16.5	16.5	—	61
	5	60.2	3.1	21.6	18.2	16.5	—	55
	16	57.5	1.3	23.4	19.1	16.5	—	55

* Not determined.

true of the hexosan removed. The results suggest the presence of a little over 5% of hexosan material removable from the cellulose by acid. On prolonged boiling this amount was somewhat increased. The hexosan does not show the same progressive removal as the xylan and the ratio of xylan loss to total loss increased with time except in the case of very dilute acids when it remained more or less constant. The material removed had not undergone complete hydrolysis to reducing sugars, though hydrolysis must have proceeded to a very considerable extent, for in only one experiment was the reducing value as much as doubled on rehydrolysis of the extract. The loss of xylan and hexosan must be ascribed largely to hydrolysis and not simply to extraction.

The results on oak cellulose given in Table VIII lead to similar conclusions. Some differences in degree are discernible and these are manifestations of the individuality of the cellulose. The xylan was rather less readily removed by very dilute acids, and whereas in oat cellulose about 5% hexosan was removed concurrently with the xylan, that fraction of the oak cellulose was more susceptible,

and seemed to be progressively attacked. With low concentrations of acid, the hexosan removed was almost equal to the xylan, the ratio of xylan lost to total loss being about 50 %. With higher concentrations this ratio increased but was not so high as that given by the oat cellulose. In another respect, too, differences were noted between the two samples of cellulose, the filtered acid extracts obtained being less completely hydrolysed in most cases.

Attempts were made to carry out a similar series of hydrolyses on a softwood cellulose, and although the removal of the xylan component could be followed accurately, it was not possible to distinguish in the dilute extracts between the mannose from the cellulosan and the other hexosan material presumably from the cellulose.

2. Extraction.

The effect of treatment of some plant celluloses with alkali was studied similarly by heating small samples for various times under standard conditions. Special precautions were needed in washing, to ensure the removal of all alkali.

Table IX. *Extraction of celluloses with boiling NaOH solutions.*

All results expressed on the basis of 100 g. original oven-dried cellulose.

Cellulose and xylan content	Conc. of NaOH %	Time	Residue	Xylan in residue	Xylan removed	Hexosan removed (diff.)	Xylan loss Total loss %
Oak (24.69)	0.1	10 min.	92.5	20.5	4.2	3.3	56
		1 hr.	89.4	18.8	5.9	4.7	56
		5 hr.	85.0	17.6	7.1	7.8	47
	1.0	10 min.	87.9	17.5	7.2	4.9	59
		1 hr.	82.2	16.6	8.1	9.7	45
		5 hr.	76.7	15.1	9.6	13.7	41
	4.0	10 min.	76.1	10.5	14.2	9.7	59
		1 hr.	72.3	8.6	16.1	11.6	58
		5 hr.	71.1	7.9	16.8	12.1	58
Wheat straw (21.52)	0.1	10 min.	94.7	18.5	3.0	2.3	57
		1 hr.	93.3	17.8	3.7	3.0	55
		5 hr.	87.4	15.3	6.3	6.3	50
	1.0	10 min.	90.7	16.3	5.2	4.1	56
		1 hr.	80.9	15.3	6.2	12.9	33
		5 hr.	66.0	8.2	13.3	20.7	39
	4.0	10 min.	80.1	10.4	11.1	8.8	56
		1 hr.	68.6	7.1	14.4	17.0	46
		5 hr.	62.9	7.0	14.5	22.6	39
Barley straw (24.04)	0.1	10 min.	84.1	14.9	9.2	6.7	58
		1 hr.	80.6	12.8	11.3	8.1	58
		5 hr.	76.5	10.4	13.6	9.9	58
	1.0	10 min.	78.9	11.6	12.4	8.7	59
		1 hr.	73.4	9.7	14.3	12.3	54
		5 hr.	68.1	9.1	15.0	16.9	47
	4.0	10 min.	72.2	6.3	17.8	10.0	64
		1 hr.	67.0	6.2	17.9	15.1	54
		5 hr.	62.8	5.6	18.4	18.8	50
Jute (14.73)	0.1	10 min.	95.1	12.2	2.5	2.4	51
		1 hr.	94.2	12.4	2.3	3.5	39
		5 hr.	90.1	11.3	3.4	6.5	34
	1.0	10 min.	93.1	12.3	2.4	4.4	36
		1 hr.	88.7	10.8	3.9	7.4	35
		5 hr.	85.3	9.9	4.8	9.9	33
	4.0	10 min.	85.7	8.6	6.1	8.2	43
		1 hr.	81.0	7.5	7.2	11.8	38
		5 hr.	80.2	7.2	7.5	12.3	38

Various concentrations of NaOH from $N/50$ to $2.5 N$ were employed but results are presented only for 0.1, 1.0 and 4.0 % each at 10 min., 1 hour and 5 hours, since these conditions adequately cover the removal of the major part of the associated cellulosan. The celluloses studied included one from a hardwood, oak, two from cereal straws, barley and wheat, and one from a fibre plant, jute, the figures for all of which are given in Table IX. Alkali as dilute as 0.1 % brought about a considerable removal of xylan even in 10 min. from all celluloses, that of barley straw being particularly susceptible. The xylan was uniformly accompanied by some hexosan. With each concentration of alkali, long boiling removed hexosan at a greater rate than xylan, as a result of which the ratio of xylan loss to total loss falls with time. Not unconnected with this observation is the fact that in effecting the same total loss a higher concentration of alkali for a short period will remove more xylan than a lower concentration for a longer period. This is well shown in the oak series, in which the residue after extracting oak cellulose for 10 min. with 4.0 % acid was 76.1 % and that with 1.0 % acid for 5 hours 76.7 %. The xylan content of the former residue was, however, 10.5 % and of the latter 15.1 %. It follows that in the preparation of xylan from cellulose, a purer extract is likely to be obtained by the use of a strong alkali solution for a short period than by prolonged boiling with a more dilute solution.

The celluloses from the four different sources showed certain distinctive differences. The jute cellulose was more resistant to extraction than any of the other samples, and the losses from jute were due more to the removal of hexosan material than xylan. The celluloses from the cereal straws provided a distinct contrast, that from barley being much more susceptible to dilute alkali than that from wheat. In proportion, however, hexosan was more easily removed from wheat, and the ratios of xylan loss to total loss are consequently uniformly lower in the wheat series. Whether such differences are characteristic of these straws has not yet been determined. The results on oak cellulose provide the basis for a comparison of the effects of hydrolysis [Table VIII] and extraction. Prolonged boiling with acids produced a progressive attack on both components, that on the xylan increasing only slightly with time. As a result, on continued hydrolysis the ratio of xylan loss to total loss does not change appreciably. In alkaline extraction, on the contrary, the removal of hexosan increased faster than the removal of xylan with the result that this ratio falls.

Discussion of hydrolysis and extraction.

Treatment of a plant cellulose with hot dilute acids or alkalis results in the removal of cellulosan to an extent which depends on the concentration and the time. Concurrently, however, there is a removal of hexosan material often to an extent considerably greater than that of cellulosan. In no case, with hot reagents, is cellulosan removed unaccompanied by hexosan. Pure cotton cellulose with dilute acids and alkalis is known to undergo only very small losses under similar conditions. There is therefore in the celluloses from woods and plant materials a hexosan fraction far more susceptible than anything in cotton. The nature of this fraction and its relationship to true cellulose on the one hand and cellulosan on the other are not yet known. The existence of such a fraction has, of course, been recognized for many years, and in the evaluation of pulps a procedure is ordinarily adopted to exclude this less resistant material. By treatment in the cold with 17.8 % NaOH, a residue is obtained termed α -cellulose, which, whilst not usually free from xylan, is taken as representing the true resistant fraction available for manufacturing purposes. Bell [1932] has shown, in a study of the methylation of this fraction, that wood celluloses do not display uniformity

as individuals. The alkaline extract, if acidified, gives a precipitate known as β -cellulose. The larger part of the material extracted is not however precipitated on acidification, and it is termed γ -cellulose, the amount being obtained by difference. These fractions have never been critically investigated. It is unlikely that the proportions of α -, β -, γ -cellulose have any absolute significance since their isolation rests on a purely arbitrary procedure. The β - and γ -fractions presumably include the material removed by dilute acids and alkalis as described in this paper.

From these experiments certain limited deductions as to the nature of this less resistant hexosan can be made. It is apparently as easily removed by dilute alkalis as is the cellulosan and further is readily hydrolysed by dilute acids to give reducing sugars. True cellulose is little affected by dilute alkali or acids. The resistance of true cellulose to hydrolysis by acids is unusual, even amongst polysaccharides, and has never been satisfactorily explained. This property is presumably connected with the immense chain length of the cellulose molecule, but not with its micellar arrangement, for regenerated celluloses, of inferior organized structure, are not markedly more susceptible to acid hydrolysis. The inference is therefore that this less resistant hexosan fraction of such celluloses is of much less molecular size, and possibly of the same order or chain length as the associated xylan, the properties of which are virtually indistinguishable. This hexosan fraction might perhaps be more properly regarded as a cellulosan, instead of as a portion of the true cellulose, in which case the cellulosan of such materials as described above would have two components, a xylan and a glucosan, and in this be analogous to the cellulosan of the Gymnosperms, which consists of mannan and xylan. Such a distinction is however one of nomenclature only, and does not explain the nature of the material. The mechanism which produces the celluloses of plant materials and woods seems to be less perfect in its achievement than that of the seed hairs of the cotton plant. In the latter, the fibres are composed of molecules of great chain length and of the same general order of magnitude, so that the properties are uniform. In the former, molecules considerably shorter in length appear to be laid down with the longer true cellulose chains. These shorter molecules would comprise the less resistant hexosan material removed concurrently with the xylan fraction.

C. THE EFFECT OF DESTROYING MOLECULAR ORIENTATION.

The physical and mechanical properties of cellulose depend not only on the nature of the molecule, but on the state of aggregation of the molecular units. The fact that the molecules are oriented in one direction and stabilized laterally by secondary valency forces gives longitudinal strength. If cellulose be dissolved in one of the suitable solvents and subsequently precipitated, this regularity of arrangement is lost, and mechanical strength largely disappears. If cellulosans are present and are retained by secondary valency forces, the effects of disturbing the regularity of arrangement in such a cellulose should be an increased availability of the cellulosan fraction owing to the extensive reduction of forces operating laterally. This phenomenon has been observed in the case of the cellulosan of wheat straw cellulose. Two methods of solution were employed, in cuprammonium solution and by formation of the xanthate with CS_2 and alkali. A large preparation of the cellulose from wheat straw was made and, while wet, was divided into three portions. In view of observations on the effect of heat drying, it was decided to make comparisons of the regenerated cellulose both in a wet and oven-dried condition. One third of the cellulose was dissolved in cuprammonium solution by prolonged shaking, filtered free of lumps which were

broken up in a mortar until smooth, and the combined cellulose solution reprecipitated by pouring into a large volume of water containing more than sufficient HCl to neutralize all the ammonia present. The gelatinous precipitate obtained was washed by decantation and on a filter till free from copper. Half the product was then dried overnight at 100° and the remainder kept wet. The portion of the original cellulose for solution as a xanthate was treated with water and alkali to give a concentration of 17.5 % NaOH. CS_2 was stirred in, and the cellulose went slowly into solution to give a light yellow opaque liquid. It was diluted with 10 % alkali and kept overnight, giving then a clear red-brown viscous solution. The cellulose from this was regenerated by precipitation in a large bath of dilute H_2SO_4 and Na_2SO_4 , a slow stream of the xanthate being run in from a tube of about 0.4 cm. diameter. In this way the cellulose was obtained in spongy irregular strings. After very thorough washing the product was divided into two portions, one being oven-dried and the other kept wet. The third portion of the original cellulose for use untreated as a control was similarly divided. In this way, six samples were obtained, untreated cellulose, wet and dried, cuprammonium cellulose, wet and dried and xanthate cellulose, wet and dried.¹ For comparison with these, similar series were prepared from two other celluloses not containing any cellulosan. One was a high-grade unbleached cotton yarn and the other filter-paper (Whatman No. 1). The origin of the cellulose of the latter was presumably wood, all the cellulosan having been removed by drastic acid and alkali treatment.

These samples were each given a number of treatments selected as a result of previous work for their suitability in providing information on the susceptibility of the cellulosan fraction. The treatments were:

- (a) 0.25 % NaOH
- (b) 1.0 % NaOH
- (c) 0.25 % H_2SO_4
- (d) Water: 2 boils for 20 min. each.
- (e) 3 % sulphite: 2 boils for 20 min. each.
- (f) 4.0 % NaOH: standing for 1 hour at room temperature.

The furfuraldehyde yield of the residue was determined on all wheat cellulose samples, both untreated and regenerated, and the reducing value of the extract from the two acid treatments.

The regenerated wheat celluloses from the cuprammonium and xanthate treatments were not identical in composition with the untreated wheat cellulose. In each case the basis of the solvent is an alkali, in the one ammonia (sp. gr. 0.920), and in the NaOH initially 17.5 % and later reduced to 13 %, as a result of which some of the xylan becomes extracted, and though reprecipitated on acidification is in a very fine condition and is carried away in the repeated washing that is necessary. This is particularly true of the cuprammonium product which reprecipitates in a highly dispersed condition. As a result, the xylan content of the xanthate product from wheat was 15 % and that of the cuprammonium rather less than 10 %, whilst the original cellulose contained 21.5 %. Such differences in xylan content might have invalidated the results had not the magnitude of the changes been great. The results of the extractions of wheat cellulose and its regenerated products are given in Table X, and those for cotton cellulose and filter-paper in Table XI. The results are expressed on 100 g. of the

¹ I am much indebted to my colleague Dr S. H. Jenkins for his assistance in the preparation and reprecipitation of the cuprammonium and xanthate celluloses used in this work.

Table X. Extraction of wheat cellulose and regenerated celluloses.

All results except $\frac{\text{xyylan loss}}{\text{total loss}}$ expressed on 100 g. of the cellulose stated (oven-dried basis).

Treatment	Xylan in				Xylan loss				Xylan in				Xylan loss			
	Residue		Total loss		Residue		Total loss		Residue		Total loss		Residue		Total loss	
	Wet: untreated. Xylan = 21.52 %				Wet: cuprammonium. Xylan = 9.53 %				Wet: xanthate. Xylan = 15.03 %							
Water	95.4	20.4	1.1	3.5	23	87.5	2.0	7.5	5.0	60	85.9	4.1	12.0	2.1	85	
	88.3	18.3	3.2	8.5	28	85.2	2.1	7.4	7.4	50	82.8	3.1	11.9	5.3	69	
	82.5	16.2	5.3	12.2	30	83.4	1.1	8.4	8.1	51	78.2	1.6	13.5	9.3	59	
	90.6	16.7	4.8	4.6	51	87.6	1.4	8.1	4.3	65	84.2	4.1	11.0	4.8	69	
	88.1	13.8	7.7	4.2	64	84.2	1.2	8.3	7.4	53	79.4	1.7	13.3	7.3	65	
3 % sulphite	95.0	20.5	1.0	4.0	21	88.0	2.8	6.7	5.3	56	85.3	4.4	10.6	4.1	72	
	81.2	8.3	13.2	5.6	70	81.4	0.4	9.1	9.5	49	81.6	1.1	13.9	4.4	76	
Dry: untreated																
Water	96.7	19.6	1.9	1.4	59	86.4	3.4	6.1	7.5	45	87.3	4.0	11.0	1.7	87	
	81.0	15.5	6.0	13.0	31	80.0	2.8	6.7	13.3	33	81.9	3.0	12.0	6.1	66	
	78.0	14.4	7.1	14.8	32	76.0	1.7	7.8	16.1	32	78.2	1.5	13.5	8.3	62	
	88.3	15.4	6.1	5.6	52	86.8	3.6	5.9	7.3	44	84.2	2.9	12.1	3.6	77	
	84.4	11.2	10.3	5.3	66	77.9	2.5	7.1	15.0	32	78.7	1.3	13.7	7.6	64	
3 % sulphite	92.4	18.8	2.8	4.8	36	84.8	4.7	4.8	10.4	31	86.2	4.3	10.7	3.1	78	
	77.5	5.2	16.3	6.2	73	79.2	1.1	8.4	12.4	40	81.5	1.0	14.0	4.5	76	
Dry: cuprammonium																
Dry: xanthate																

cellulose concerned, and because of the losses of xylan in the course of preparation of the cuprammonium and xanthate products are not directly comparable with one another. Instead, the relative effects of the different treatments and the nature of the materials removed by those treatments must be compared.

Table XI. *Extraction of cotton cellulose and filter-paper and their regenerated products.*

Results expressed on 100 g. cellulose (oven-dried basis).

Treatment	Cotton cellulose						Filter-paper		
	Untreated		Cuprammonium		Xanthate		Filter-paper		
	Air-dried	Oven-dried	Wet*	Oven-dried	Wet	Oven-dried	Untr. air-dried	Cupr. wet	Xanth. wet
0.25% NaOH	94.2	92.0	89.0	92.9	97.3	95.6	97.1	96.8	95.1
1% NaOH	94.1	91.1	88.7	91.8	96.6	92.9	95.4	94.9	95.1
0.25% H ₂ SO ₄	94.4	93.2	87.3	95.5	98.4	93.3	97.8	98.2	95.2
2.5% H ₂ SO ₄	93.8	91.8	83.1	91.0	95.5	92.9	96.3	92.4	93.5
Water	98.3	95.1	93.9	97.3	98.6	95.9	98.8	99.1	95.8
3% sulphite	97.0	93.0	89.9	95.2	98.0	93.3	97.4	97.3	93.8
4% cold NaOH	96.5	95.3	96.6	96.3	98.7	96.8	97.6	97.3	95.2

* This sample was very gelatinous and became highly dispersed on subsequent treatment, so that some loss occurred on filtration.

The results on the wet xanthate-regenerated cellulose are more striking than those on the cuprammonium cellulose because less xylan was lost in the method of preparation. The differences between the various extracting and hydrolysing agents were smoothed out as a result of regeneration in both cases, so that hot water removed almost as much xylan as any other reagent, in marked contrast to

Fig. 3. Removal of xylan from untreated and regenerated cellulose.

its action on the untreated cellulose (Fig. 3). No equivalent increase in availability of hexosan material occurred. This is in accord with the results obtained on the celluloses not containing cellulosan given in Table XI. Neither filter-paper nor cotton cellulose on solution and reprecipitation showed any significant change in susceptibility to these various treatments.

The dried samples were very similar in properties to the wet, save that superimposed upon the changes brought about by solution and reprecipitation was also the effect of exposure to heat previously described. This appeared to be smaller in the regenerated celluloses than in the untreated material.

DISCUSSION.

It is believed that the cellulosan fraction of natural celluloses is retained by secondary valency forces. The association is, however, stronger than this type of linkage would normally provide. Additional stability is provided by the orientation of the cellulose molecular chains and their arrangement in micellae. If it is presumed that the cellulosan molecules are similarly oriented and distributed throughout the micellae, not necessarily only on the surface, then such an aggregate might be expected to have the properties of the natural celluloses as shown in this paper. A portion of the cellulosan may very readily be extracted with alkali in the cold, yet even prolonged heating with alkali fails to effect a complete extraction. This has long been a matter of comment. Heuser & Haug [1918], investigating a cereal straw cellulose, showed that many extractions with hot 6 % NaOH resulted in a loss of only 80 % of the xylan, and that even after drastic treatment under pressure at 140°–150°, 5–6 % of the xylan remained. Similar results were obtained with the wheat cellulose used in this work. The xylan content, initially 21.5 %, was reduced only to 5 % by prolonged boiling with 10 % NaOH, a loss of less than 80 %. The hydrolytic effect of acid treatment is capable of removing this resistant fraction easily, and 3 % H₂SO₄ at 100° for one hour eliminated this 5 % residue. The distribution of xylan molecules through the micellae would account for such differences in extraction.

On the solution of the cellulose and subsequent reprecipitation the organized arrangement is largely destroyed, and the secondary valency forces between the cellulose and xylan molecules are no longer operative. As a result, the xylan becomes easily removable by reagents which previously had little effect upon it. In the untreated and oriented condition about 5 % of the xylan only was water-soluble. After modification so that orientation was impaired nearly 80 % of the xylan was removed under the same conditions. Cold 4 % alkali then extracted well over 90 %, a result that could not be achieved on the untreated material, even by prolonged boiling with alkali of higher concentration. No significant increase in the susceptibility of any hexosan material occurred, this change in properties being confined to the xylan.

SUMMARY.

1. The cellulose of most plants and woods differs from that of cotton in containing associated polysaccharides, known as cellulosans, which are tenaciously retained and must be considered as an integral part of the cellulose aggregate.

2. Heat-drying produces some change in the properties of both components of such a cellulose, which is manifest in an increased availability to extracting and hydrolysing agents.

3. The effect of heat treatment may be observed repeatedly on the same sample and must involve breakage of the cellulose chains, though the xylan fraction is affected to a much greater extent.

4. Preparations of the water-soluble material produced as a result of heat-treatment are mixtures which can be partially separated to give a portion of higher xylan content. Some oxidation undoubtedly occurs, and uronic groupings are present.

5. The xylan may be removed from celluloses by treatment with either acid or alkali, but a concurrent loss of hexosan material takes place in all cases.

6. In acid hydrolysis there is no apparent break in the continuity of the reaction. The reducing value of dilute acid extracts indicates that the material removed is not completely hydrolysed to reducing sugars.

7. Continued boiling with alkali removes hexosan at a greater rate than xylan, and in effecting the same total loss a higher concentration of alkali in a short period extracts more xylan than a lower concentration for a longer period.

8. Plant celluloses show considerable differences of behaviour towards hydrolytic and extracting agents and reveal distinct individualities.

9. By solution and reprecipitation of a cereal cellulose, the organized molecular structure may be destroyed, with the result that the xylan, which was initially extracted only to a small extent by water and dilute alkali, becomes almost completely soluble. No equivalent change in the properties of the hexosan material occurs.

10. These observations are in accord with the view that the cellulosan fraction of the cellulosic aggregate of plant materials and woods is oriented and participates in the micellae, being retained by secondary valency forces identical with those which obtain between parallel cellulose chains in pure cotton cellulose.

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