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CHEMICAL STRUCTURE IN THE HEMICELLULOSE GROUP

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Summary

The polysaccharides that accompany cellulose in the plant cell wall consist mainly of xylans, glucomannans, arabogalactans and related polymers containing residues of L-*rhamnose. The xylans are of various types, all of which have as a common feature chains of* β-*1,4'-linked xylopyranose residues. To these are attached as side-chains various residues including, amongst others,* L-*arabofuranose,* D-*glucuronic acid, 4-0-methyl-*D-*glucuronic acid, 2-(*β-D-*xylopyranosyl)-*L-*arabofuranose,* D-*galactose,* L-*galactose. The xylans differ amongst themselves in the nature of the side chains and in their relative proportions. From the marine algae, another type of xylan has been isolated having both* β*1,3'- and* β*1,4'-linked xylose residues in the main chain. Consideration is given also to the main structural features of some galactomannans, glucomannans and arabogalactans that accompany xylans in many groups of cell wall polysaccharides.*

It is difficult to define the term hemicellulose and, fortunately, as our knowledge of this group of substances increases and the assignment of individual names based on their chemical structure becomes possible, there is less and less occasion to attempt an impossible task. In general, the name is applied to a group of carbohydrates found in the cell walls of plants, mainly in associa-

tion with lignin. Chemically, they show little relationship to cellulose and, so far as the function of the commonest of them is understood, they seem to provide, together with lignin, an amorphous phase enveloping the cellulose strands and giving strength to the cell walls. Little is known of the manner in which these three components are bound together, whether by purely physical forces of interaction or partly by these and partly by chemical links, perhaps of the ester type. Some observations made in the course of enquiries into the extraction of the hemicellulose components from woody materials have a bearing on this problem, but the matter will not be considered further, since the present paper deals primarily with the structural relations which have been found to exist between certain members of the hemicellulose group. In some instances, these cell-wall polysaccharides may serve as energy reserves for the plant.

Many methods have been used to separate the hemicelluloses from the cellulose and lignin with which they are associated and complicated systems of classification have been put forward based on the nature of the solvent used for extraction. These have proved to be of little value and are now rarely used. In general, the polysaccharides of the hemicellulose group may be removed from lignified tissue by water (which is effective in special cases only) or by aqueous sodium hydroxide before or after removal of the lignin by the chlorite or some alternative procedure. The treatment to which the plant material has been subjected before extraction of the hemicelluloses is attempted has a marked effect on the extent of the separation that can be effected.

In general, the hemicelluloses can be isolated by precipitation from aqueous solutions by the addition of alcohol. They are then obtained as amorphous solids, which consist of mixtures of polysaccharides that can be separated only with great difficulty. Some fractionation can often be effected, however, by precipitation of insoluble copper complexes when these are formed or by fractional precipitation by ammonium sulphate from aqueous solution. The component polysaccharides appear to be of comparatively low molecular weight in general (D.P. not greater than 150). The sugar residues of which they are composed include D-xylose, L-arabinose, D-glucuronic acid, 4-O-methyl D-glucuronic acid, D-galactose, L-galactose, D-mannose, L-rhamnose and L-fucose. Such a wide range of components, several of which may be present in one molecule, leads to considerable difficulty in the elucidation of molecular structure and not many years ago the task appeared to be almost insuperable. The situation has been changed very materially, however, by the introduction of chromatography, which has made it possible to operate classical methods of attack on the micro scale and has rendered available a

new and extremely powerful procedure in the shape of partial hydrolysis studies. In this way, a polysaccharide may yield a series of di-, tri- and oligosaccharides, the structures of which tell much about the arrangement of the residues in the original molecule. Up to the present, enzymic methods, with one or two notable exceptions, have not been so useful as they have been with other groups of polysaccharides.

In view of their chemical interest and their industrial importance, the hemicelluloses have been intensively studied during the past few years and general patterns of molecular structure are now becoming apparent. It is of interest to note that in the lignin groups, with which the hemicelluloses are so closely associated in nature, the general pattern of molecular structure is now in sight, following the recognition by Freudenberg[1] that coniferyl alcohol and similar substances may be converted enzymatically into free radicals from which are formed the polymerising units present in natural lignins. There is evidence also that the precursors of lignins are carbohydrates, which by a complex series of changes undergo transformation into the aromatic alcohols by way of shikimic acid.[2] It is apparent, therefore, that the pathways which lead from simple carbohydrates to hemicelluloses on the one hand and to lignins on the other are very different, despite the intimate association of the two groups of materials in the cell wall.

One of the most important of the families of substances to comprise the hemicelluloses is that based on xylose residues. The xylans constitute a high proportion of the woody tissues of plants and their behaviour is therefore of special interest to the paper manufacturer. For this reason, the xylan portion of esparto grass has been selected for structural studies from the early days of carbohydrate chemistry. It can be extracted by alkali and purified with relative ease by precipitation in the form of its copper complex. Methylation studies then showed that, on hydrolysis of the methylated derivative the main product was 2,3-di-0-methyl D-xylose, pointing to the presence of a chain of 1,4′-linked D-xylose residues, which must be in the β-form in view of the low specific rotation of the polysaccharide. The early end-group studies

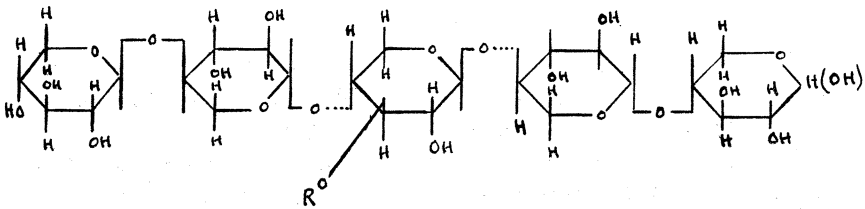


Fig. 1—R = H or possibly a chain of 1,4′-linked xylose residues

were difficult to interpret owing to the presence of some L-arabofuranose residues,[3] but it was shown in due course that fractions could be obtained from esparto xylan containing no arabinose residues.[4] The evidence obtained by a study of this material pointed to a molecular structure of the type shown in Fig. 1.

The main structural feature is the backbone of 1,4′-linked β-D-xylose residues. End groups in the form of xylopyranose residues are present to the extent of 1 for every 40 xylose units. Indications were obtained of a molecular weight corresponding to a degree of polymerisation of about 80 units, pointing to a singly branched molecular structure. From the isolation of 2-0-methyl xylose on hydrolysis of the methylated xylan, it would appear that the linkage at the branch point is of the 1,3′-type. It is possible, however, that in general the backbone of xylose residues in the xylans is unbranched and further evidence is required on this problem.

This backbone of 1,4′-linked xylose residues is a general feature present in the great majority of xylans. They vary amongst themselves, however, in innumerable ways by the attachment of one or more residues of other types to the xylose units of the backbone. This attachment may occur through C_2 or C_3 of one of the xylose units and a wide variety of other sugar residues has been identified as taking part. The one most commonly found is, perhaps, the L-arabofuranose residue, attached as a single terminal unit, usually through C_3 of one of the xylose residues of the main chain. In esparto xylan, the proportion of L-arabinose varies from nothing in the material mentioned above to a high percentage.[5] Substances still richer in arabinose content have been isolated by Perlin[6] from wheat flour. Similar materials have also been isolated from barley flour and rye flour. Here, some of the xylose residues of the main chain have arabofuranose residues linked to C_2 and C_3, giving rise to a structure of the type shown in Fig. 2.

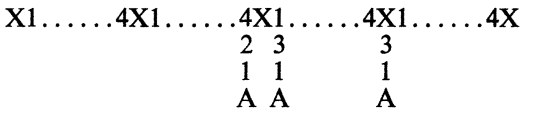


Fig. 2

These numerous arabofuranose residues can be split off by partial hydrolysis and the product is an arabinose-free xylan very like the xylan fraction from esparto that has already been discussed.

Other xylans are known in which no arabinose residues are present. Normally, however, some other residue is present, a case in point being a xylan which can be isolated from the cell wall of ripe pears.[7] This has a branched

structure (Fig. 3) containing some 120 sugar residues, the novel feature being the presence of one D-glucuronic acid residue per molecule, the linkage being through C_3 of one of the xylose residues.

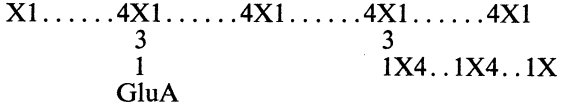


Fig. 3

Many xylans contain more than one type of residue attached to the main xylose chains. Examples of this are to be found in the xylans present in cereal straws. For instance, in wheat straw xylan, which has been intensively studied by groups of workers in Canada, France and Great Britain,[8] both L-arabofuranose and D-glucuronic acid side chains are present in a structure of the type indicated in Fig. 4.

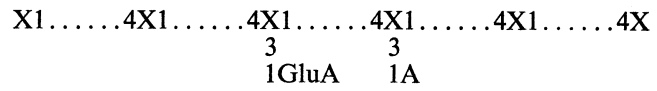


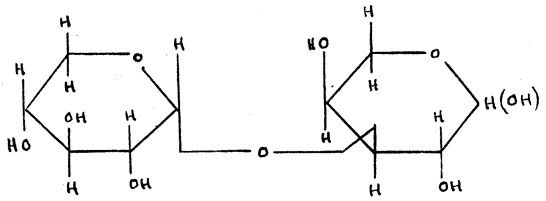
Fig. 4

Here again, fractions can be separated having very different arabinose contents, ranging from zero to very nearly one arabinose for every xylose residue and the naturally occurring material is clearly a mixture of closely related substances, all of which are built on the same general pattern. The content of uronic acid residues is here about 4 per cent. They are mainly units of D-glucuronic acid, but some 4-0-methyl D-glucuronic acid may be present also. Proof has been given that these uronic acid residues are combined directly with C_3 of a xylose residue in the main chain. Evidence has also been obtained of the attachment of the L-arabinose residues to the main chain of xylose residues. This follows from a study of the oligosaccharides obtained from the xylan by the action of a pentosanase enzyme present in *Myrothecium verrucaria*.[9] This readily attacks X1-4X links, but has no effect on the A1-3X linkage and it has been shown that amongst the products of hydrolysis there are oligosaccharides in which arabofuranose residues are linked directly to xylose. The molecular size of the wheat straw xylans as they exist in the plant is not known with certainty, but there is evidence that the molecular weight of some fractions which have been examined by physical methods is small (D.P. *c.* 50). It may well be, however, that in the plant fractions much higher molecular weights are present.

It is possible, but not yet certain, that the main chain of xylose residues in the wheat straw xylan may be branched and this applies also to the corre-

sponding xylans from barley and oat straw. The general pattern of structure is the same in all three groups of xylan, with a series of molecules containing more or less arabinose residues, together with some uronic acid units. In the case of oat straw, there is evidence that some at least of the uronic acid residues are united to the main chain of xylose residues by 1,2′-links.[10]

Still further complications have been encountered in studies of the hemicelluloses present in various parts of the maize plant.[11] For example, in the group of xylans which can be extracted from corn hull, there are found,



Xα1 - 3A

Fig. 5

besides xylose, residues of L-arabinose, L-galactose and D-galactose, together with a small proportion (3 per cent.) of uronic acid residues. Whistler and his colleagues have obtained from this material after partial hydrolysis the disaccharide (Fig. 5; 3-0-α-D-xylopyranosyl-L-arabinose), which on isolation has the arabinose residue in the pyranose form. It is more than likely, however, that in the polysaccharide the arabinosyl unit possesses the furanose ring structure. This disaccharide has been found also amongst the products of partial hydrolysis of a xylan present in gum from golden apple (*Spondias Cytheria*)[12] and in the mucilage from cress seed[13] and it would appear that the grouping Xα1-3A1.... may be of common occurrence as a side chain attachment in polysaccharides. It is to be noted that, in contrast with the usual occurrence of β-D-xylosyl residues, the residue is here present in the α-form.

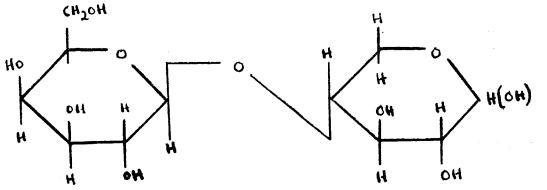
Along with the disaccharide (Fig. 5), a most unusual trisaccharide has been isolated from the products of partial hydrolysis of maize hull xylan. This contains residues of L-galactose, L-arabinose and D-xylose and it has been shown to have the structure (Fig. 6; L-galactopyranosyl-(1->4)-D-xylopyranosyl-(1->2)-L-arabinose), in which the L-galactopyranose residue is linked to C_4 of a xylose residue, which itself is linked to C_2 of a residue of L-arabinose.

L-Gal 1 — 4X1 — 2A

Fig. 6

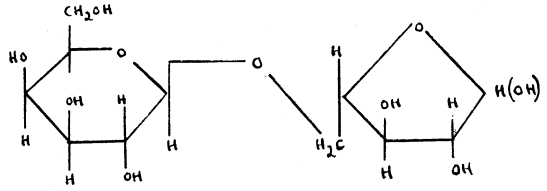
Once again, the arabinose portion reverts on isolation to the pyranose form, but the trisaccharide is presumably linked glycosidically to the main chain of xylose residues through C_1 of the arabinose in its furanose form. On examination by the methylation procedure, the polysaccharide gave rise, after methylation and hydrolysis, to 2:3:4:6-tetra-0-methyl DL-galactose, proof being thus afforded of the presence of terminal units of D-galactose, as well as of L-galactose.

Other neutral substances obtained by the partial hydrolysis of corn hull hemicellulose are the disaccharides 4-0-β-D-galactopyranosyl-D-xylose (Fig. 7), 5-0-β-D-galactopyranosyl-L-arabofuranose (Fig. 8) and 4-0-β-D-xylopyranosyl-D-xylose. Glucuronic acid residues are present also and these are united to the main chain through C_2 of a xylose residue, as is indicated by the isolation of the aldobiouronic acid 2-0-α-D-glucuronosyl-D-xylose. Methylation studies have shown that all the galactose (both D- and L-) is present in the form of terminal units in a highly branched polysaccharide, in which the galactose residues are linked to the main structure in at least three different ways.



Galβ1 - 4X

Fig. 7



Galβ1 - 5A(f)

Fig. 8

Yet another picture is presented by the xylans of the corn cob. From these, Whistler and his colleagues[14] obtained by the method of partial hydrolysis a series of oligosaccharides of the general formula in Fig. 9, proof

$$X1 — (4X1)_n — 4X$$
(n = 0 to 6)

Fig. 9

being thereby given of the presence of sequences of β1,4′-linked xylopyranose residues in the polysaccharide. Side chains consisting of arabofuranosyl residues (A1....) are linked to the main chain, probably by 1,3′ linkages; there are end groups of xylopyranose residues (X1....) and a possibility that glucose residues may also be present. Residues of D-glucuronic acid and of 4-0-methyl D-glucuronic acid are encountered linked to C_2 of certain of the xylose residues and some glucuronic residues have been found united to xylose by a linkage of the type 1,4′. In the latter case, the chain — or side chain — would appear to be terminated by the grouping of Fig. 10, which has been isolated, after partial hydrolysis of the xylan, in the form of the corresponding reducing trisaccharide.

GluAα1 — 4X1 — 4X1.....

GluA = D-glucuronic acid

Fig. 10

It may be noted that residues of the disaccharide 2-[β-D-xylopyranosyl]-L-arabinose (Xβ1-2A) are found in the xylans from corn cobs, from esparto and from barley husks and it would appear that in some of these xylans the main chain of xylose residues is terminated by grouping other than a normal xylose residue.

Of perhaps greater interest still in papermaking are the hemicelluloses of woods. The general picture is one of extreme complexity, since the cell-wall materials of wood are usually composed of hemicelluloses of several different types. In addition to members of the xylan group, there are polysaccharides based on galactose and on mannose and, in addition, there are mixed types that comprise as main features of their structure two or more sugar residues. Examples of these are to be found in the glucomannans and the galacto-arabans. Problems of isolation and purification are particularly troublesome and, although much work has been carried out on wood hemicelluloses during the past few years, very little in the way of unique structural assignment has been achieved. Most of the information has come from partial hydrolysis of mixtures of polysaccharides and, whilst this gives details concerning some of the structural units present in the macromolecules, it is not yet possible to piece these together into the form of definite molecular structures.

In one or two instances, the investigations have been carried to a further stage. For example, detailed structural studies have been made on a xylan that can be extracted from beechwood[15] by dilute alkali without previous delignification.[16] This contains residues of xylose and of 4-0-methyl-D-glucuronic acid, together with a trace of L-rhamnose, probably not structurally significant, but no arabinose is present in the molecule. The 4-0-methyl

D-glucuronic acid is joined to a xylose residue in the main chain by a linkage of the type 1:2′ and it is possible to picture the main structural feature of this xylan as a chain of some 80 β-1:4′-linked D-xylose residues, with a terminal xylose residue and with side chains of 4-0-methyl-D-glucuronic acid attached, on the average, to every tenth xylose residue by a 1:2′-link (Fig. 11).

X1.....4X1.....4X1.....4X1.....4X
2
1MGluA

MGluA = 4-0-methyl-D-glucuronic acid

Fig. 11

Hemicelluloses from softwoods are usually highly complex mixtures of polysaccharides from which it is difficult to separate individual substances. In contrast with xylans from hardwoods, they contain arabinose residues, together with mannose, rhamnose and possibly other sugar residues. The isolation of xylobiose and 2-0-α-(4-0-methyl-D-glucuronosyl)-D-xylose by partial hydrolysis of the xylans from *Picea nigra* and *Pinus sylvestris* indicates that the softwood xylans may be similar in their general structure to beechwood xylan. There is evidence[17] also that, in some softwood xylans — for example, those from Monterey pine (*Pinus radiata*) and Maritime pine (*Pinus pinaster*) — linkages of uronic acid residues occur through C_3 of a xylose unit. This is shown by the identification of 3-0-α-(4-0-methyl-D-glucuronosyl)-D-xylose (Fig. 12) amongst the products of partial hydrolysis of the hemicellulose from *Pinus radiata*, when it is found together with the aldobiouronic acid 2-0-α-(4-0-methyl-D-glucuronosyl)-D-xylose (Fig. 13). It will be recalled that the same 1,3′-linked aldobiouronic acid occurs as a component residue in the xylan of wheat straw.[8]

MGluA1 — 3X
Fig. 12

MGluA1 — 2X
Fig. 13

More detailed studies[18] have been undertaken on a hemicellulose from the Norway spruce (*Picea excelsa*). This was extracted from the delignified wood by dilute aqueous alkali and the xylan portion of the complex mixture of polysaccharides was separated by precipitation of the contaminating materials as the copper complexes. Two xylose-rich fractions were obtained, which contained no arabinose residues. These gave an hydrolysis xylose and a uronic acid that was shown to be 4-0-methyl-D-glucuronic acid. Examination of one of these fractions by the methylation procedure showed that the following residues were present in the xylan — X1...., ...4X1...., $\overset{2}{4}$X1.... and MGluα1 – 2X^{4}_{1}..... On the basis of this and collateral

evidence, it was concluded that xylan has a straight chain of 80-85 1:4′-linked β-D-xylopyranose residues, every fifth unit of which, on the average, carries a terminal 4-0-methyl-D-glucuronic acid residue linked through C_2 (Fig. 14). It is likely that this xylan is one of many closely related molecular types present in the wood. It very closely resembles in structure the xylan from

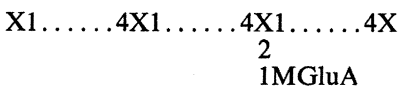


Fig. 14

beechwood,differing only slightly in the proportion of uronic acid side chains and in the number of xylose residues in the molecule.

The absence of arabinose residues is to be noted despite the fact of their general occurrence in softwood hemicelluloses. Some of the arabinose is known to be present in arabogalactans such as the ε-galactan of the larch and the arabogalactan of the Jeffrey pine. It is, however, already clear that some softwood xylans[19] are structurally similar to those from cereal straws and esparto in containing arabinose residues as well as uronic acid residues attached to the main xylose chain. The general picture is therefore very similar over a wide range of xylans present in woody tissue from gymnosperms and angiosperms.

Although differing in detail, the xylans mentioned above have had one common feature, namely, a main chain composed of β1:4′-linked xylopyranose residues. Some xylans, however, are known to have a different structure in which xylopyranose residues mutually linked in the 1:3′ position and in the 1:4′ position occur in the same main chain. An example showing this novel feature is the xylan that occurs in considerable quantities in the red seaweed *Rhodymenia palmata*.[20] This contains xylose residues only and, as the result of methylation experiments, it has been shown to be composed of residues of X1...., ...4X1...., ...3X1.... in the proportions of 1:12:3, respectively. The main features of the molecular structure can be represented therefore by Fig. 15, the number of X residues per molecule being about 17. Further work

Fig. 15

will be required to establish the order in which the 1:3′ and 1:4′-linked residues occur. This algal xylan is an analogue of the glucose polysaccharide lichenin, present in Iceland moss, in which glucose residues with 1:3′ and 1:4′-linkages occur in the same main chain.

Many other polysaccharides occur in the cell walls of plants and it must suffice to mention here one or two examples to illustrate the general structure patterns. To one of them, the galactomannan named guaran, which can be extracted from guar, a definite and unique structural formula can be assigned as the result of work by Whistler and his collaborators.[21] Partial hydrolysis gave several products, amongst which were the disaccharides Mβ1-4M (M= mannopyranose) and Galα1-6M and the trisaccharides Mβ1-4Mβ1-6M and Galα1-6Mβ1-4M. The isolation of these substances, taken in conjunction with the results of methylation and other experiments, leads to the assignment of a molecular structure (Fig. 16) in which there is a main chain of β-1:4′-linked mannopyranose residues, with side chains of Galα1.... residues attached to C_6 of every alternative mannose residue. As in the glucose group of polysaccharides, main chain linkages of the 1:4′-type seem to be a common feature of mannans.

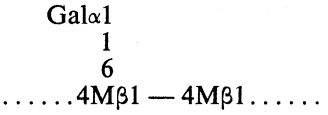


Fig. 16

The detailed structures of the mannose-containing polysaccharides of the softwoods have not yet been fully established, but it is known that these polymers contain 1:4′-linked β-D-mannopyranose residues as the dominant structural feature. Thus, the main products of the hydrolysis of the methylated glucomannans from Loblolly pine (*Pinus taèda*)[22] and Sitka spruce (*Picea sitchensis*)[23] woods are mixtures of 2:3:6-tri-0-methyl-D-mannose and 2:3:6-tri-0-methyl-D-glucose. Since partial acid hydrolysis of the glucomannans gives rise to oligosaccharides containing both mannose and glucose residues in addition to oligosaccharides containing only mannose residues, it is clear that a glucomannan is present. It is possible, however, that this polysaccharide is only one of a range of closely related species with differing proportions of 1:4′-linked mannose and glucose units.

Much less is known concerning the detailed molecular structure of the arabogalactans, which are frequently found along with xylans and mannans in the cell-wall polysaccharides of softwoods. One of these, the so-called ε-galactan from larch wood (*Larix decidua*) has been the subject of considerable effort, both in the U.S.A. and in this country.[24] Its structure has however proved to be extremely complex and, although something is known of the types of residue present in the molecule, no unique structural formula can yet be advanced. One of the difficulties is that the material as isolated appears to

contain many molecular species, differing from each other in the relative proportion of arabinose and galactose residues. Another serious complication is the recent discovery that arabopyranose residues form part of the molecule.[25] On partial hydrolysis, the disaccharide 3-O-L-arabopyranosyl-L-arabinose is produced, pointing to the presence of structural units of the type Ap1 – 3Af1..... Since the arabopyranose residues occur as end groups, these units are probably attached as side chains. In addition, there may be side chains of arabofuranose residues (Af1....) of the kind encountered in the xylan group. The backbone of the molecule would appear to be a chain of galactopyranose units, some (or perhaps all) of which are linked in the 1,3′ positions and to this there are attached side chains of one or more galactopyranose residues, the linkages being mainly 1,3′, but possibly in some cases 1,6′. To this assembly must be added units of Ap1 – 3Af1.... and possibly of A1..... The possibility cannot yet be ruled out that some of the chains may contain both arabinose and galactose residues and it is clear that much further work will be needed before a satisfactory molecular structure can be put forward.

If the definition of the hemicelluloses as cell-wall polysaccharides is accepted for the time being, many other polysaccharides could be included in this survey. Notable examples are the so-called cereal gums,[26] which are present in small amounts in barley and other grains. They are polysaccharides of high molecular weight, the one from barley being composed entirely of β-glucose residues. It is of special interest in that half of these residues are linked in the 1:3′-position and the other half by 1:4′-links. The precise order in which these two linkages alternate in the long unbranched chain is not yet known.

Still further examples of cell-wall polysaccharides are to be found in alginic acid and the many sulphated polysaccharides of highly complex structure present in the algae. There are also the complex mixtures — not as yet unravelled — of polysaccharides containing residues of glucose, mannose, galactose, xylose, arabinose, rhamnose, fucose and uronic acids, found in the lignified tissues of plants, but the examples cited may suffice to give some idea of the problems that face the chemist in this wide and evergrowing field. It is all too clear that only a slight beginning has been made in the elucidation of detailed structures and there can be no doubt that all the resources of modern techniques will be required to overcome the formidable difficulties that lie ahead.

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DISCUSSION

PROF. H. W. GIERTZ: The question has been discussed earlier today whether the total material in the fibre is just a mixture of cellulose chains and hemicellulose chains or whether we have to consider two separate phases. The last point was raised by Prof. Frey-Wyssling a long time before the electron microscope was in operation. His idea was that we had certain cellulose strands or microfibrils in the fibre and that these were embodied in a matrix of hemicellulose material. As I understand it, Prof. Hirst is of much the same opinion.

Other aspects have been argued in the last 10-15 years. It has been said that the fibre wall (S2) is more or less a homogeneous body with a pronounced tendency to split longitudinally (in the same way as asbestos does) and that the microfibrils are not natural units but artefacts, the size of which depends on the intensity of the grinding or ultrasonic treatment; that the cellulose and hemicellulose molecules are blended very much into each other and are partly co-crystallised; and that the cellulosic material occurs in an overlapping amorphous/crystalline system without sharp borderlines. Thus, the wall of native fibres should be fairly homogeneous, like a viscous rayon filament and regions of different densities go continuously over into each other. I would like to discuss this point today, mixing a little the physical and chemical aspects of the problem.

At the Fibre Chemistry Section of the Swedish Forest Products Research Laboratory, we attacked the problem by treating delignified spruce fibres mainly in two different ways — by partial acid hydrolysis and by fractionated dissolution.

1. When treating a cellulosic material with hot dilute acids, as suggested by Nickerson, one part of the material is very rapidly hydrolysed, whereas the rest is attacked only slowly. By following the reaction kinetically, the amount of the easily accessible regions of the fibre can be calculated. We have performed this experiment on the same pulp, but with varying acids (2 – 5 N HCl; 3.5 N HCl + 0.6 M $FeCl_3$; 2 – 4 N HBr; 3 – 7 N H_2SO_4) and at different temperatures; in all cases, the same amount of accessible material was obtained. This was taken as an indication that the borderline between accessible and non-accessible regions must be rather sharp. The amount of non-accessible material in a series of different spruce sulphite pulps was always 42 — 43 per cent. of the wood, whereas the accessible part varied 5 — 21 per cent. of the wood, depending on pulp quality.

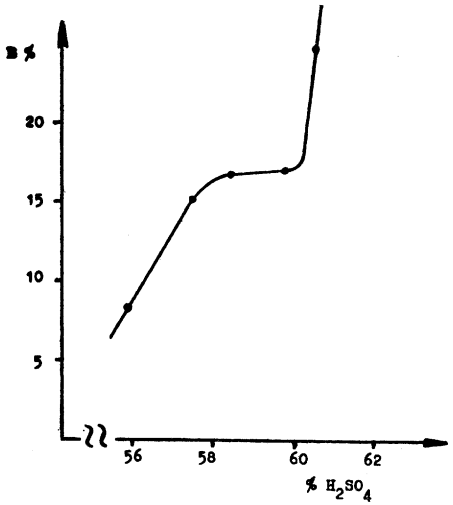

Fig. H — Strong sulphite pulp extracted with sulphuric acid — amount of extracted material against acid concentration

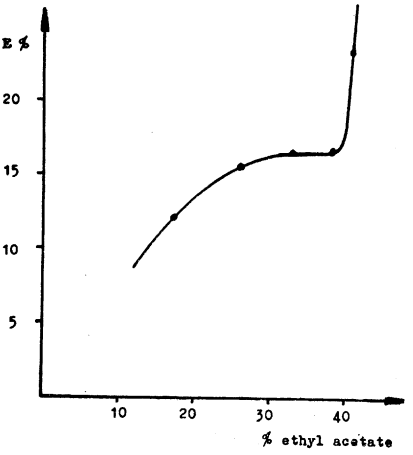

Fig. J — Nitrated strong sulphite pulp extracted with mixtures of ethyl alcohol and ethyl acetate — amount of extracted material against solvent composition

2. Cellulose fibres swell considerably in sulphuric acid in the concentration range 50 — 58 per cent. At the same time, parts of the cellulosic material dissolves, as shown in Fig. H. The interesting feature in this dissolution process is that the amount of dissolved material increases with the acid concentration up to about 56 — 57 per cent. sulphuric acid solution, but then levels out despite the fact that the dissolving power of the acid is continuously increased with the concentration. At about 59 — 60 per cent., the rest of the cellulosic material dissolves. At this point, the swelling changes from interfibrillar to intrafibrillar in nature. This treatment is nothing but a fractional dissolution and, not being continuous, it seems to divide the fibre material in two main fractions. The resistant part amounts to about 42 per cent. of the wood in different spruce sulphite pulps, whereas the easily soluble part varies according to pulp yield.

3. Exactly the same feature is obtained when a nitrated sample is treated with mixtures of ethyl alcohol and ethyl acetate of different composition, as shown in Fig. J. In this case, the solvation power is continuously increased with increasing ethyl acetate content of the solvent. In the region 65/35 parts per volume ethyl alcohol/ethyl acetate, however, dissolution ceases and increases markedly again at a mixture composition of 60/40, which shows

that the dissolution in this case too is typically fractionated. The resistant part corresponds to 42 per cent. of the wood.

In all these experiments, the cellulosic material has been separated into two main fractions, of which the resistant part amounts to 42 per cent. of the spruce wood. It must be kept in mind that the fractionation technique, however, has been essentially different in the three cases. Hydrolysis attacks and degrades the material continuously and quantitative estimation is based on the difference in reaction velocities for the two fractions. The treatment with sulphuric acid involves no chemical attack, but a strong interfibrillar swelling and partial dissolution. The same is the case with the nitrated fibre, but here the fractional dissolution has been performed on a derivative and not on the native fibre.

This separation into two main fractions becomes more interesting when the fractions are analysed for their chemical constituents. The resistant part consists mainly of glucan (Table 1), whereas the accessible part is a mixture of polymers of glucose, mannose and xylose.

TABLE 1

Chemical composition of the resistant fraction

Treatment	*Pulp*	*Yield of wood, %*	*Chemical composition, %*		
			Glucose	*Mannose*	*Xylose*
3.5 N HCl, 95°C	Strong sulphite	40.0	99	0.5	0.5
59% H_2SO_4	Strong sulphite	41.2	94	4	2
57% H_2SO_4	Rayon grade sulphite	41.0	96.5	2	1.5
65/35 ethyl alcohol/ ethyl acetate denitration	Nitrated strong sulphite	41.8	100	nil	nil

From these experiments, we have drawn the conclusions that the cellulosic material in spruce wood fibres is composed of two discrete fractions, the borderline between which is relatively sharp, excluding extensive transition areas. The resistant part consists of pure cellulose and, taking the results of modern electron microscope investigations into consideration, constitute the microfibrils. This fraction is the *true cellulose* and it amounts to about 42 per cent. in spruce wood. Consequently, the accessible material constitutes the interfibrillar substance. It seems to consist mainly of glucomannans and xylans, so there is good reason to keep the old term *hemicellulose*

for this fraction. In wood, there are other hemicellulose compounds such as galactan, araban, glycuronans and pectic substances. As these wood polyoses, part of which are laid down in the middle lamella, are extremely accessible, they do not occur in technical pulps.

From a practical point of view, the main difference between cellulose and hemicellulose is not because of chemical composition, but is their physical nature. The cellulose of the microfibrils is highly crystalline; it does not swell in water and chemical attack is a surface reaction. In contrast, the interfibrillar hemicellulose, probably owing to its heterogeneous composition, is of an amorphous nature; it swells in water and is easily accessible to acids and other chemical agents. It seems likely that the microfibrils also contain disordered, X-ray amorphous regions to some extent, but these are much denser than is the interfibrillar hemicellulose.

DR. B. G. RÅNBY: Prof. Hirst commented upon the relationship of the strength of a bond between glucuronic acid and a xylose unit, which has been well known to us for the last four or five years. The question is whether a carboxyl group — on the sixth carbon atom, for example — can increase the rate of hydrolysis of a cellulose chain. The point was that the glucosidic bond on one side of the glucuronic acid unit could be strengthened, but we do not know about the strength of the bond on the other side. If it is so easy to isolate the aldobiouronic acids from a xylan by hydrolysis, this could be so because the bond between the glucuronic acid and the xylose is so much stronger, but it may also be so because the adjacent bonds in the xylan chain are so much weaker — that is, easier to open by hydrolysis. I do not wish to stress this point about the influence of carboxyl groups, because the chains also contain some residual aldehyde groups resistant to oxidation by sodium chlorite. These groups might also influence the stability of the cellulose chains.

MR. J. R. SIMMONS: I notice that Dr. Jörgensen has only given carbohydrate analyses of the 5 per cent. caustic soda extracts. I wonder if he has carried out any such analysis on the 10 per cent. caustic soda extracts? We have carried out such analyses at various strengths and, at about 10 per cent. caustic soda concentration, we have found something rather different. Besides mannan and xylan, we get an appreciable amount of acid-precipitable matter, which appears to be degraded cellulose, since the hydrolysate consists essentially of glucose. We have found that this acid-precipitable degraded cellulose fraction from the 10 per cent. caustic soda extract has a detrimental effect on the strength properties of the pulp rather greater than the beneficial effect of the natural hemicellulose content of this

extract. The larger the amount of this degraded cellulose fraction, the weaker the pulp will be in general.

DR. L. JÖRGENSEN: For the pulps described in the paper, we have not analysed any 10 per cent. fraction, but a few 18 per cent. fractions — I do not think anything more is gained by plotting solubilities in 10 per cent. caustic soda against strength properties. We have plotted the ordinary alpha-cellulose contents against the strength factors and obtained curves similar to those shown.

DR. G. O. ASPINALL: We found, in carrying out structural investigations of the hemicellulose group, that there is a certain amount of the glucomannan fraction that is, to all intents and purposes, similar to cellulose and is extracted by approximately 10 per cent. alkali. It comes out with the glucomannans, but thereafter it becomes insoluble. We have examined one such fraction and, so far as we can see, it is quite indistinguishable from normal cellulose, except for the difference that it is of lower molecular weight.

PROF. GIERTZ: When I spoke some minutes ago about the resistant and the soluble parts of the fibre, I did not want to go into the general problem of alkali solubility, because the swelling and solution phenomena are much more complicated in this case.

In Fig. K (*a*)–(*d*) are shown some typical alkali solubility curves. The analysis has been performed according to CCA 8:55 and the PE fraction (beta-cellulose) has been precipitated in cold solution (about 0°C) with the aim of keeping the SE fraction (gamma-cellulose) in as solvated a condition as possible, thus avoiding the adsorption of the soluble substances on the precipitate. To avoid misunderstanding, I want to use the following terms. The resistant cellulose is called the R fraction and the extract the E fraction. After neutralisation, the latter is divided into precipitate and soluble extract, called the PE and SE fractions, respectively. When using 18 per cent. caustic soda solution, these fractions correspond to alpha-, beta- and gamma-cellulose.

It is of interest to note that, for all pulps examined, the SE fraction is more or less constant within a wide alkali concentration range (10 — 22 per cent. caustic soda), whereas the PE curves show typical maxima at about 10 per cent. caustic soda. Furthermore, the amount of SE in sulphite pulps decreases with cooking degree (that is, acid hydrolysis), whereas the PE fraction increases with hydrolysis and oxidation. Obviously, the SE and PE fractions must be of different natures, physically or chemically.

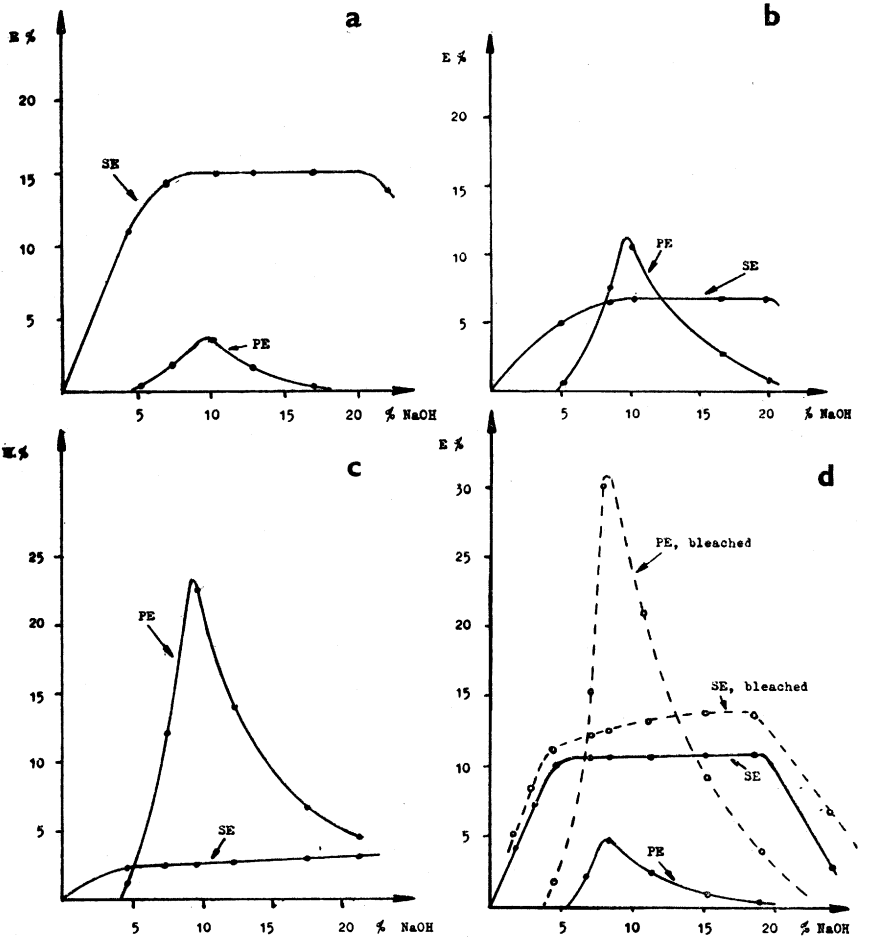

Fig. K — Alkali solubility curves — amount of soluble extract (SE) and precipitable extract (PE) as a function of caustic soda concentration

(*a*) Strong sulphite pulp
(*b*) Rayon grade sulphite pulp
(*c*) Overcooked sulphite pulp
(*d*) Paper grade sulphite pulp before and after strong hypochlorite bleaching

The fact that the amount of SE is constant within a wide alkali concentration range, independent of the swelling and dissolving power of the alkali, indicates that it is a discrete fraction and thus resembles the soluble fraction in treating native fibres with 57 per cent. sulphuric acid solution or nitrated fibres with a 65/35 mixture of ethyl alcohol/ethyl acetate, as mentioned earlier. Quantitatively, the SE fraction corresponds to the amount of soluble substance in the latter cases and chemically it consists of polymers of glucose, mannose and xylose, as shown in Table 2. There can be no doubt about it that we are dealing in these three cases with one and the same fraction of the cellulosic material; thus, the SE fraction (or gamma-cellulose) of spruce sulphite pulps is nothing but hemicellulose.

It is a well-known fact that alpha-cellulose, when isolated in the ordinary way, does not consist of pure cellulose. If, however, the analysis is performed under certain conditions, the R fraction consists of pure glucan (as is shown in Table 2) and, having a typical microfibrillar structure, it obviously consists of cellulose.

Being soluble in strong alkali, beta-cellulose is commonly supposed to belong to the hemicelluloses. This is misleading, however; no beta-cellulose occurs in chlorite holocellulose. It is formed during the different pulping and purification operations (hydrolysis, oxidation). In spruce sulphite pulps, the sum of the R and PE fractions is constant and amounts

TABLE 2

Chemical composition of the R, PE and SE fractions after alkali solubility determinations

Treatment	*Pulp (sulphite)*	*Yield of wood %*	*Chemical composition, %*		
			Glucose	*Mannose*	*Xylose*
R fraction					
15% NaOH	Paper grade	39.7	96.5	2.5	1.0
18%+18%+4% +4% NaOH	Paper grade	40.3	99	0.5	0.5
8% LiOH	Rayon grade	39.1	99	0.5	0.5
PE fraction					
10% NaOH	Paper grade	1.9	96	2	2
SE fraction					
8% LiOH	Paper grade	4.5	17.5	58.5	24
8% LiOH	Paper grade, overbleached	—	28.5	52	19.5

to 42-43 per cent. of the wood. It seems likely therefore that the PE fraction is nothing but degraded cellulose, which has been verified also by Rånby with the electron microscope. As a consequence, the PE fraction should consist of glucosan, which is the case (Table 2).

There is one thing more I want to mention about the nature of beta-cellulose. As can be seen from Fig. K (*a*)–(*d*), the PE fraction starts to appear at a concentration of about 4 per cent. caustic soda and reaches its maximum at about 10 per cent. This behaviour runs parallel with the intramicellar swelling of cellulose, changing the lattice from cellulose I to alkali cellulose (mercerisation), which phenomenon also starts at an alkali concentration of 4 per cent. and is completed within 8-10 per cent., as has been shown by Rånby in X-ray and moisture regain studies. It is tempting therefore to suspect a connection between mercerisation and the formation of the PE fraction. In Stockholm, we have been able to show that the PE fraction always shows the typical and very sharp X-ray pattern of alkali cellulose, whereas the R fraction shows the pattern of cellulose I with no trace of the lines of alkali cellulose, when isolated with 4 per cent. and 6 per cent. alkali solution. The lines of alkali cellulose first start to appear at a concentration of 8 per cent. caustic soda.

From this experiment, we have drawn the conclusion — though still not definitely proved — that the formation of the PE fraction is a direct consequence of the intramicellar mercerising swelling. This swelling must involve appreciable forces within the microfibril and, if this has been weakened by hydrolysis or oxidation at some spots, it seems likely that the swelling stresses will cause the fibril to break at these weak points. The short fibril fragments formed will peptise as such in the alkali solution; but, after neutralisation, they will easily precipitate because of the hydrophobic nature of crystalline cellulose.

Looking at the problem in this way, the beta-cellulose is an artefact and is of no primary interest when dealing with papermaking pulps. Its amount is certainly an indication of the degree of degradation that the microfibrils have been subjected to, but this effect can more easily and more accurately be measured by an ordinary viscosity determination.

Summing up, the alpha-, beta- and gamma-cellulose analysis gives quite a lot of information about the cellulosic material. When dealing with papermaking pulps, however, the gamma-cellulose value is of greatest interest, because it gives the amount of hemicellulose in the pulp. The alkali solubility (the sum of beta- and gamma-cellulose) is obviously of no interest.

It should be pointed out that analytical methods based on solubility in sodium (or potassium and lithium) hydroxide solutions are not ideal, the main disadvantage being that mercerisation takes place before optimum hemicellulose dissolution occurs, which makes a separation into PE and SE fractions necessary.

This kind of fractionation is more complicated when dealing with sulphate pulps and birch pulps.

MR. L. G. COTTRALL: Do I understand Prof. Giertz correctly that he thinks beta-cellulose is produced during the extraction and not during the pulping process? From the practical point of view, does it really matter whether the pulping process actually breaks off little bits and pieces or whether it merely weakens some of the stuff so that bits and pieces are produced when you carry out the extraction?

PROF. GIERTZ: You are quite right, the $beta_{10}$ fraction certainly indicates the amount of attack. The problem, however, is that the PE curve always has a very sharp peak around 10 per cent. caustic soda, but is not always exactly at the same concentration. Thus, it seems difficult to develop a simple and accurate method. I think it will always be easier to get a value for the degree of degradation by an ordinary viscosity determination.

MR. COTTRALL: We are dealing here, I think, with two effects. We have the building up of strength, because of the natural hemicellulose in the pulp, which does contribute towards the strength, although maybe only up to a certain value in hemicellulose content. Then you have the deterioration of the cellulose, if it has deteriorated during the pulping process, which reduces the strength. You have the balance of those two factors. I think that is what Mr. Simmons means. I do not think he means that the strength goes down always when the extract of caustic soda is high at 10 per cent. Sometimes the strength is high at 10 per cent. extraction and sometimes it is lower.

MR. P. E. WRIST: I should like to ask Prof. Giertz why the amount of extractable material that is precipitable decreases when you exceed 10 per cent. alkali.

PROF. GIERTZ: Because the swelling and dissolving properties of the sodium hydroxide solution are highest at 10 per cent. You do not get better swelling properties by increasing the concentration. When this is done, the water is taken up so much by the sodium hydroxide that the swelling power falls. With sulphuric acid, however, this does occur and, with the

mixture of ethyl acetate and alcohol, the swelling power increases progressively with the amount of acetate.

THE CHAIRMAN: I think that this question of the relationship of hemicellulose content to strength is a very important one. I was particularly impressed by the concluding sentence of Dr. Jörgensen's paper, which seemed to swing the pendulum back to the time I entered the industry some 25 years ago, when it was believed that the physical condition of the cellulose might have a good deal to do with the physical qualities of the paper.

PROF. GIERTZ: It is an old experience of papermakers that the higher the hemicellulose content, the stronger the paper or, the higher the pentosan content (as it was known in the 1930s), the better the strength. This relationship holds well for sulphite pulps. The very important question is, however, whether this is a primary correlation, involving cause and effect or only a secondary phenomenon.

As pointed out by Dr. Jörgensen today, we have always to remember that sulphite cooking means acid hydrolysis. Hydrolysis is needed to liberate and dissolve the lignosulphonic acid and, at the same time, the hemicelluloses are partly saccharified and the cellulose attacked and degraded, which latter means a weakening of the cellulosic framework and lower fibre strength. Thus, during a sulphite cook, the weakening of the fibre will always run parallel with hemicellulose dissolution. Paper strength has been related to the hemicellulose content, but it might as well be to fibre strength — this is the factor determining the optimum paper strength.

DR. RÅNBY: The effect of the hemicellulose will be further discussed tomorrow in connection with the beating of fibres. From what we know about beating today, especially when you have seen the latest pictures from the Forest Products Research Laboratory in Stockholm of the fibre-to-fibre bonds in paper, it seems reasonable to assume that it is largely a question of making the fibres so soft that the bonding surface, fibre-to-fibre, can be increased in size and you can get more effective hydrogen bonding from one fibre to another. The plasticising effect in a wetted pulp fibre is largely related to the content of the hemicellulose. If you bring that aspect in, you do not have to assume that the hemicellulose makes the glue in the paper; it is only that its presence makes the beating so much more possible. If you do not find so much fibrillation in beating, the main effect would be to make the whole fibre so much softer.

PROF. GIERTZ: I agree exactly. The amount of hemicellulose definitely has an effect on how readily the pulp is beaten. We are now coming, however,

to such matters as swelling, water imbibition, fibrillation and fibre flexibility, on which the hemicelluloses seem to have a considerable effect.

MR. H. W. EMERTON: We must resist the temptation to explain the effect of hemicelluloses in black and white terms. It seems to me unlikely that this is purely chemical or purely physical: almost certainly both effects are present. What we are trying to do this week is to find where to put the emphasis.

There is one aspect that has not been touched upon. It was pointed out by Jayme and von Köppen (*Das Papier*, 1950, **4** (19/20) 373; (21/22), 415; (23/24), 455) that under certain cooking conditions — chiefly those obtaining in sulphite digestion — the surface layers of the fibre are weakened by hydrolysis. Extensive bonding may occur between the surface layers of adjacent fibres, but, because the surface layers are not well anchored to their parent fibre, the whole interfibre link may be comparatively weak.

DR. F. MULLER: The impression that I get from this discussion is that softwood acid sulphite pulp is rather a poor material for studying the influence of hemicelluloses on the strength properties of paper. The experience we have had with strawpulp in this respect, I think, is much clearer and shows the hemicelluloses have a preponderant influence on the strength of paper-making pulps.

Since I read a paper on this subject last year in London (*Tappi*, 1957, **40** (6), 470), I do not think it is necessary to refer at length to our results, but I wanted to point out this difference as well as the further difference with the hardwood pulps studied by other workers.

PROF. B. STEENBERG: I have very much enjoyed listening to the talks today, but I am rather surprised that nobody has mentioned what happens if you take a highly purified cellulose fibre and proceed with graded methylation of it to see how its papermaking properties change. I think that reference to work of that type would be of some interest for those who advocate the extreme importance of the hemicelluloses in the cellulose group. Why does nobody talk about it?

THE CHAIRMAN: Prof. Steenberg has thrown down the challenge. Would either of the original speakers like to reply to it?

PROF. STEENBERG: Well, that is a good enough answer for me.

MR. EMERTON: Is Prof. Steenberg asking what the effect of substitution of hydroxyl groups is?

PROF. STEENBERG: No, we know that. I thought everyone knew that if you take a highly purified pulp having very poor papermaking qualities and partially methylate it, increased swelling and better strengths result. An increase in the number of methyl groups passes through a maximum until methyl cellulose is finally obtained, which does not swell in water at all and has no papermaking properties. Introduction of a group that obviously requires some space, opens up the structure, making it more bulky. Swelling can take place and bonding comes as a result. When there are too many of these groups, the material becomes hydrophobic and swelling diminishes. Here is a case of something not native in the material like hemicellulose, but something added later; the added groups — not capable of hydrogen bonding — open up the structure and make it possible for water to penetrate. Loose ends get into the tacky state and bonding can occur, but it is not due to a specific tacky material.

I thought this observation, well known to most of you, was very difficult to harmonise with any assumption that a specific group (or a specific carbohydrate type) would be the only important substance for beating, etc. In short, it very much corroborates Dr. Jörgensen's idea.

THE CHAIRMAN: That has cleared up a point of which the audience were perhaps more in ignorance than Prof. Steenberg thought.

MR. WRIST: I wish to take up the question of the importance of hemicelluloses in pulp strength, particularly the proposition that increasing the one inevitably results in an increase of the other. The use of additives to a pulp affords a method of studying the effect of amount of adhesives in a pulp without changing the fibres in other respects. I believe that many of the commercial additives such as guar gum or starch derivatives approximate sufficiently in behaviour to hemicelluloses to allow this generalisation.

Such a test on a variety of hardwood pulps, softwood pulps and groundwood, prepared by a wide variety of pulping and bleaching methods, has failed to reveal any trend so simple as that proposed. Contradictions were many, even between pulps of a similar type. In many instances, especially in the case of strong softwood pulps, additional bonding resulted as evidenced by increased burst and tensile strengths and loss of opacity. These changes were of the same order as could be achieved by small additional beating and no other advantage was realised.

Very weak pulps were relatively insensitive to the addition of adhesives. Weak softwood pulps and most hardwood pulps, however, did not exhibit any such common trends. Cases were obtained of improvements in strength

exceeded by those obtainable by additional beating; others have even shown losses of strength, particularly of tearing and folding strengths, without improvements in tensile or bursting strengths.

I would prefer to say that hemicelluloses or other adhesives enhance bonding, but whether or not increased hemicellulose proves advantageous to paper strength is dependent on many other factors such as fibre flexibility, fibre surface strength, extent of degradation of the fibre structure during pulping and bleaching and the strengths of the fibres themselves.

DR. RÅNBY: On this question of the hemicellulose content and its effect upon the colloidal properties of the fibres, we did some work about five or six years ago using colloidal sols of cellulose micelles in aqueous solution (*Faraday Soc. Disc.*, 1951, **11**, 158). It was shown that one could easily coagulate and precipitate these cellulose sols by adding small amounts of electrolytes. The cellulose micelles were classified as hydrophobic colloids. One could also stabilise the sol against precipitation with electrolytes by adding extracted hemicellulose in water or just as well by adding water soluble cellulose derivatives like carboxymethylcellulose (CMC) or ethyl hydroxyethylcellulose (Modocoll). These experiments show that one action of hemicellulose on cellulose is that of a protective colloid. Hemicellulose can apparently be replaced by water soluble cellulose derivatives. In this way, we apply a concept from classical colloidal chemistry.

MR. G. F. UNDERHAY: I was very interested in Prof. Giertz' references to the usefulness of density as well as strength measurements and I could not help thinking when Dr. Jörgensen referred to Schopper-Riegler data that it was rather like introducing a mongrel to a Cruft's dog show. The Schopper-Riegler determination of freeness is a bad method of measuring a property that, in any case, is mainly incidental and is not essential to finished paper properties and I felt a little bothered whether that was the right thing to do. I should be glad to have Dr. Jörgensen's comments.

DR. JÖRGENSEN: I agree that it is better to have sheet densities against strength factors instead of °S.R. or any other similar measurement. In this case, however, we found that the comparative picture did not change and decided to use the most common method — that is, to plot the strength properties at a certain level of beating measured as °S.R. against the amount of material soluble in alkali.

MR. D. MCNEILL: Is there any way other than beating to treat pulp to give good sheet formation? Could the addition of a small amount of rayon pulp

reject, such as Prof. Steenberg was talking about, which is near enough to pure cellulose, followed by wet rolling as on an MG cylinder give the same effect in density as in beating without using so much power?

PROF. GIERTZ: There are some pulps it is not necessary to beat to obtain high paper strength. One kind is the sulphate pulp studied by Jayme and co-workers, which is obtained by cooking quite fresh spruce wood by the ordinary sulphate process (Jayme, G., Kohler, L and Haas, W. L., *Das Papier*, 1956, **10** (21/22), 495). Such pulps have been called biological pulps. The unbeaten pulp shows the following paper strength characteristics — breaking length 8 700 m., tear factor 390 and 21 000 double folds, of which the latter two especially are extremely high.

Another type of pulp is that obtained by cooking spruce or pine with a slightly acidified sodium sulphite liquor (pH 6 – 3; 170°c). Despite the fact that the yield is about 65 per cent., delignification has been extensive enough to allow complete separation of the fibres as in the ordinary sulphite cook and no special machine is needed as in the semichemical process (Bölviken, A. and Giertz, H. W., *Norsk Skogind.*, 1956, **10** (10), 344).

Judging from the high yield figure, it must be expected that some of the hemicelluloses from the middle lamella are present on the fibre surface. The unbeaten pulp has the same slippery feel as a highly beaten greaseproof pulp has and the paper strength properties are quite high — breaking length 8 300 m., tear factor 107 and 2 800 double folds.

I think that every one of us will agree that some hemicellulose or some other swollen substance — maybe in a very thin layer — is needed on the surface of the fibre to produce the effect of gum or glue. Ordinary acid sulphite and sulphate pulps seem to be lacking such surface substances and therefore we have to beat them perhaps with the aim of removing the primary wall and thus disclosing fresh internal surfaces. In the case of the pulps just mentioned, however, the fibre surface seems to be covered with hemicellulosic material. Characteristic of the biological pulps is that the paper strength decreases markedly at the very beginning of beating, then increases again and that the high strength is lost on drying the pulp.

PROF. G. CENTOLA: Dr. Jörgensen closed his paper by quoting a sentence from an article that Dr. Borruso and I published about 8 years ago and presented at the second congress of A.T.I.P. in Paris.

I will repeat the reasons that led us to emphasise structure modifications, especially the surface structure modifications, instead of underscoring chemical composition.

The amount of the chemical constituents determined by analysis is an average value of the total fibrous mass. On the other hand, the chemical constituents fraction that is directly involved in the beating process and consequently contributes to the formation of fibre-to-fibre bonds is only located in the outer surface layers.

About 10 years ago, I had the opportunity of reading some papers in which an attempt was made to correlate the amount of hemicelluloses present in some pulps and the behaviour of such pulps on beating. Generally, the experiments were carried out by preparing a series of pulps characterised by different amounts of hemicellulose by extraction with alkali at various concentrations. The effect of hemicellulose extraction on pulp properties did not seem right — or only to some extent. I thought it necessary, first of all, to take into consideration other phenomena related to structure changes. In fact, repeating the same experiments on cotton linter pulps, we obtained changes in pulp properties very similar to those observed for the woodpulps when beating was related to the alkali concentration in the extraction.

It is well known that above certain concentrations the alkali can act so that the fibres become inert to beating action. Apart from the structure changes, it is necessary to consider not only the distribution of the substances that accompany the cellulose in the fibre, but also the state of combination in more or less sensitive complexes to the swelling and plasticising action of water. This consideration, together with other of our tests on the tendency of cellulose to delaminate have led us to direct our studies to plasticising fibres obtained either by modifying the structure or by introducing substances able to increase the rate of beating by favouring the swelling of the cellulose lamellae and consequently the cleavage of the fibre. We will refer to these arguments in our paper for session 4.

DR. F. L. HUDSON: I want to draw attention to the paper by M. N. Fineman (*Tappi*, 1952, **35** (7), 320). He was dealing with wet strength and proved, so far as the paper went, that urea- and melamine-formaldehyde resins did not produce wet strength in pulps that were substantially free from hemicellulose. Even cotton contains sufficient hemicellulose to be important in this respect, as he showed that extraction with caustic soda prevented it reacting with resins to give wet strength to the paper.

Is there any evidence that any particular hemicellulose or hemicelluloses in general are likely to react readily with amino resins or to react with formaldehyde?

MR. F. BRIDGE: Some time ago, I was concerned with a similar problem, though not with the production of wet strength in paper: I was asked to

provide pulps with varying lignin contents. This presented the problem of removing the lignin without touching the hemicellulose material. I resorted to the holocellulose method, which, I think it is generally agreed, leaves only the carbohydrate fraction. It was found that wet strength was definitely a function of the lignin content and not of the hemicellulose content.

Samples of a fairly raw-cooked sulphate pulp were subjected to different degrees of treatment with sodium chlorite and a range of pulps prepared in stages of decreasing lignin content. These pulps were then made into standard sheets incorporating a urea-formaldehyde resin for the wet-strengthening process. As the percentage of lignin in the pulp decreased, so did the retention of resin and the wet strength, until with a pulp of zero permanganate number the retention was virtually nil. (A full account of this work will be found in *Proc. Tech. Sect. P.M.A.*, 1947, **28**, 239: Schofield, G. and Harrison, H. Ainsworth, 'Some factors affecting the retention of amino resins by woodpulps'.)

PROF. GIERTZ: I wish to take up another point in this discussion on the hemicelluloses. If a researcher wants to show that paper strength depends on the hemicelluloses, of course, he needs to make a pulp without any hemicellulose to see if it is possible to get good paper strength from it.

The easiest way to get rid of the hemicelluloses is to extract the pulp with 10 or 18 per cent. sodium hydroxide solutions. By such treatment, the hemicelluloses are more or less fully extracted, but, at the same time, quite a number of other things happen to the pulp. When treating with a sodium hydroxide solution of mercerising strength, the whole cellulose lattice is changed; native cellulose I is converted to alkali cellulose; the whole fibre is extremely swollen. When washing away the alkali, the lattice of cellulose II is obtained and the fibre is still somewhat swollen. By drying, this swollen fibre shrinks and collapses and a type of fibre is obtained that is quite different from the native one. It is very dense, homogenised glassy fibre, which will not swell in water nor fibrillate on beating. When native fibres are beaten, opacity decreases; with this type of fibre, however, the opacity increases, which shows that cutting takes place, but no hydration. Hemicellulose extraction with a mercerising solution has thus formed quite a new kind of pulp, therefore all experiments based on comparisons with this kind of fibre are of no value.

MR. A. R. SMITH: I should like to make one comment about this question of applying amino-formaldehyde resins. The mechanism of the production of wet strength by this method is not understood and I think it is not at all

clear whether it is necessary for the resin to be within the cellulose structure or whether the mechanism is an external one of bonding the fibres together.

It must be appreciated in a case like this, when it is found that wet strength has not been produced under certain conditions, that it may be because the affinity of the resin for the cellulose has been lost or because the resin is not having the same effect on the cellulose as it does under normal conditions. So, to say that, because the hemicellulose has been removed, the resin is no longer effective may not be the full story. It should be appreciated that the resin may not have been picked up by the pulp at the stage of addition and, therefore, although resin was originally added to the pulp suspension, it may not be present in the final paper. Unless this is known (and I am not acquainted myself with Fineman's paper), it would appear that we must look further to find the explanation of the phenomena observed.

DR. W. GALLAY: It so happens that I assisted in directing the work of Fineman reported. This was not a question of resin pick-up, but rather one of the strength of the bridge between the amino-formaldehyde and the fibre through the hemicellulose.

DR. MULLER: Fibre cellulose consists of very long chains united in a more or less crystalline lattice and, therefore, they are not easily detached. The hemicellulose chains are much shorter and not arranged in a crystalline structure and so they are more easily detached. You need some detachment of these hemicellulose or other chains to obtain sufficient hydrogen bonding for the fibre-to-fibre bond strength of the paper. In my opinion, that is what is actually done in beating.

Another thing comes into play and that is, if you illtreat a fibre sufficiently, either by hydrolysis or by some other means (perhaps, some oxidation process, especially in an alkaline medium), the cellulose may be broken down and its lattice structure loosened so much that there is some detachment of the cellulose chains as well, so that it can take up the role of the hemicellulose. There is no prior reason that a glucose β–1, 4– chain should not be able to form hydrogen bonds as well as a hemicellulose chain does. I think the same will hold good for the development of wet strength with the urea-formaldehyde resin, because this resin has to attach itself to the fibre surface. The more chain fragments that are taken out, the greater possibility there will be of the urea-formaldehyde attaching itself to the fibre.