MODEL EXPERIMENTS ON REASONS FOR DISCOLORATION DURING ACETYLATION

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INTRODUCTION

It is a well-known fact that cellulose acetate made from wood pulp has a more or less pronounced yellowish shade and gives at least slightly hazy solutions. This has been considered to be as a result of reactions of different components of wood pulp during acetylation, for instance such components as residual lignin, extractives, hemicelluloses and various kinds of degradation products. To throw some light upon the influence exerted by different carbohydrate components on discoloration during acetylation, model experiments were carried out with low-molecular weight carbohydrates as test substances. Special attention was paid to the influence of carbonyl groups in the molecules.

DISCOLORATION ON ACETYLATION OF LOW-MOLECULAR WEIGHT SUGARS

The acetylation tests were performed using an apparatus (*Figure 1*) developed and constructed at The Finnish Pulp and Paper Research Institute. This apparatus is equipped with interchangeable measuring heads

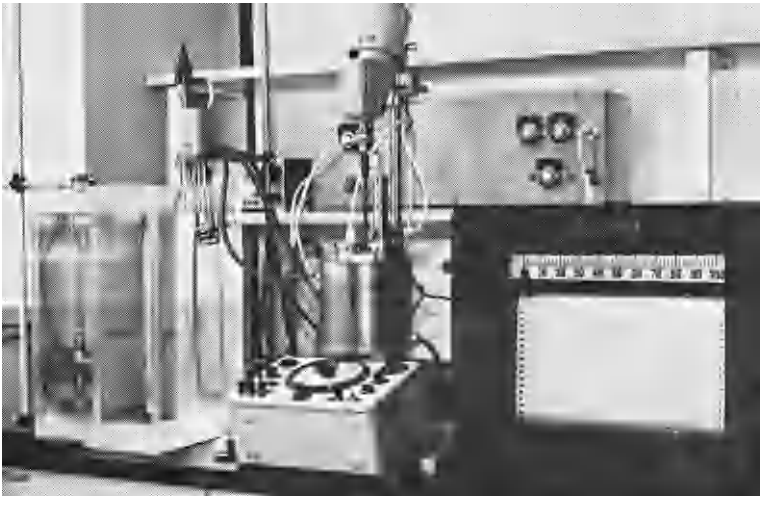

Figure 1. Acetylation equipment

which allow continuous recording of either electrical conductivity, turbidity or colour of the acetylation mixture. The amount of substrate used in each test was 2·5 g. This was activated at 38°C for half an hour in 32 g of acetic acid. Then a mixture of 50 g of acetic anhydride and 30 g of methylene chloride was added. Sulphuric acid (200 mg) in acetic acid (20 g) was used as catalyst. Thus, the composition of the acetylation mixture was: 52 g acetic acid, 50 g acetic anhydride, and 30 g methylene chloride. The acetylation temperature was 38°C.

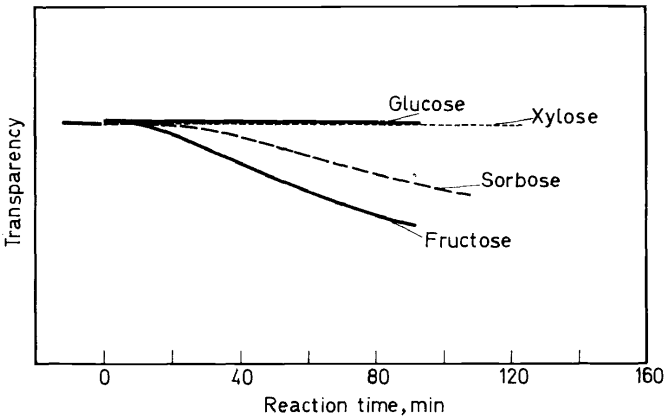

Figure 2. Transparency of acetylation mixture as a function of time. Monosaccharides

Figure 2 shows the development of colour on acetylation of different monosaccharides. Here, the transparency of the acetylation mixture is given as a function of the acetylation time calculated from the addition of the catalyst. The starting line shows the transparency level of a completely clear and colourless solution. As can be seen, no discoloration takes place in the acetylation mixture of glucose or xylose. The same holds true of mannose, galactose, arabinose, and many other compounds. Contrary

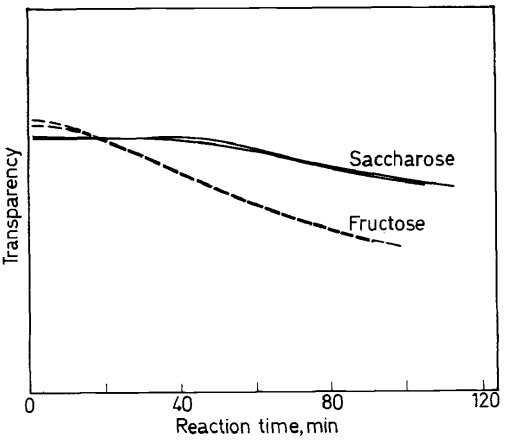

Figure 3. Reproducibility of the transparency test

to this, on acetylation of fructose or sorbose, the transparency of the acetylation mixture starts to diminish within a few minutes after the addition of the catalyst. It may be mentioned that the reproducibility of this test is excellent, as can be seen in *Figure 3.*

In the experiments on development of colour during acetylation, the monosaccharides listed in *Table 1* were tested. It can be seen that aldoses,

Table 1. Colour development on acetylation of monosaccharides

Monosaccharides		*Colour development*
Aldohexoses:	Glucose	—
	Mannose	—
	Galactose	—
Ketohexoses:	Fructose	+
	Sorbose	+
Aldopentoses:	Xylose	—
	Ribose	—
Aldonic acids:	Gluconic acid	—
Uronic acids:	Glucuronic acid	—
Sugar alcohols:	Mannitol	—
	Sorbitol	—

gluconic acid, glucuronic acid, and the sugar alcohols did not develop any colour. Contrary to this, the acetylation mixture of sorbose and in particular that of fructose was discoloured very quickly.

Figure 4 shows transparency curves for some di- and oligosaccharides. As was expected, the acetylation mixture of cellobiose remained colourless. The very low transparency value at the beginning of acetylation is obviously due to undissolved sugar, which makes the solution hazy, and hence a low transparency value is obtained. As the acetylation proceeds and the sugar becomes dissolved, the transparency of the acetylation mixture increases and after complete acetylation reaches the level of the colourless solution. On the

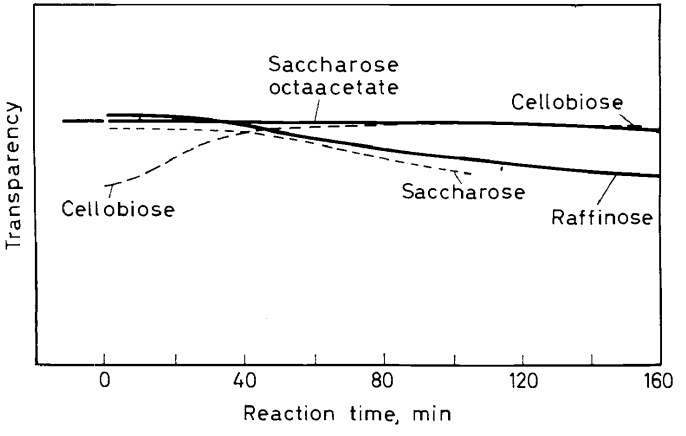

Figure 4. Transparency of acetylation mixture as a function of time. Di- and oligosaccharides

other hand, the transparency value given by the recorder can also be higher than that of a colourless solution. This may happen, when the sugar crystals are completely transparent and have highly reflecting faces. In this case the amount of light which reaches the photocell is greater than that which is obtained using a completely transparent solution.

The dope of saccharose is discoloured much more slowly than that of fructose or sorbose in *Figure 2*. Obviously the fructose unit of the saccharose molecule is not available for the discoloration reaction. As the inversion of saccharose proceeds, thus liberating the fructose units available for this reaction, the acetylation mixture turns dark. On the other hand, saccharose octaacetate seems to be quite stable to the discoloration reaction. This indicates that the acetyl groups either stabilize the glycosidic bond of saccharose or they make the liberated fructose units resistant towards the discoloration reaction.

It may be pointed out that neither xylose nor mannose developed any colour in the acetylation mixture. This indicates that if xylan or mannan is responsible for the discoloration during the acetylation of wood pulp, they must have undergone some kind of conversion during the pulping and bleaching processes.

INFLUENCE OF BLEACHING TREATMENTS UPON MONO- AND DISACCHARIDES

Since the acetylation of xylose and mannose as such does not cause any colour formation, a study was made of the influence on discoloration exerted by different treatments employed in connection with bleaching of dissolving pulp. Thus, several monosaccharides were subjected to hot alkali treatment and chlorine dioxide treatment respectively under the conditions shown in *Table 2*. After these treatments, the solutions were analysed by paper chromatography.

Table 2. Conditions on treatment of sugars

	Hot alkali treatment	*ClO_2 treatment*
Sugar concentration (%)	12	12
Amount of chemical (%)	8 (NaOH)	0·6 (av. Cl)
Temperature (°C)	95	70
Time (h)	2	3

The chromatograms were eluted with the mixture ethyl acetate–pyridine–water (8:2:1) and sprayed with naphthoresorcin which gives characteristic blue spots with aldoses and red brown ones with ketoses (shaded spots). Chlorine dioxide was found to have no effect on the sugars. Some of the results of hot alkali treatments are given in the following chromatograms.

Figure 5 shows the results for the hot alkali treatment of glucose and mannose. The lines 1, 3, and 5 are references showing the positions of glucose, mannose, and fructose. No. 2, the alkali treated glucose shows, in

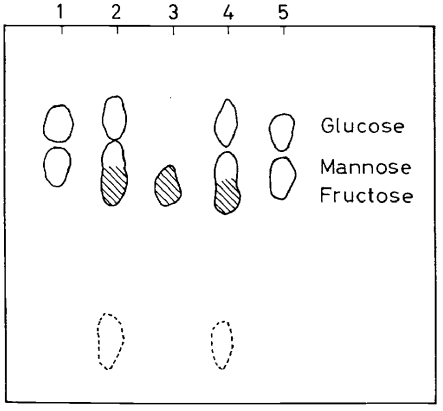

Figure 5. Chromatogram, elution time 24 h [1, Glucose and mannose; 2, Hot-alkali-treated glucose; 3, Fructose; 4, Hot-alkali-treated mannose; 5, Glucose and mannose]

addition to the characteristic glucose spot, distinct spots of mannose and fructose. On line 4, the presence of fructose and glucose in alkali treated mannose is evident.

As can be seen from *Figure 6*, alkali treated xylose gave, in addition to the spot of xylose, only two very weak spots, one of which being arabinose. However, as the R_f-values of keto sugars are considerably higher than those of the corresponding aldoses, an experiment was carried out with a very

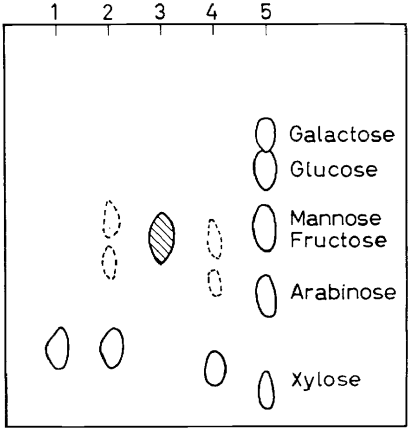

Figure 6. Chromatogram, elution time 24 h [1, Xylose; 2, Hot-alkali-treated xylose; 3, Fructose; 4, Hot-alkali-treated xylose; 5, Galactose, glucose, mannose, arabinose and xylose]

short elution time. This revealed a new distinct spot of a keto sugar with an R_f-value almost twice as high as that of xylose. This is seen in *Figure 7*, in which the lines 2 and 4 correspond to alkali treated xylose.

The results obtained from chromatographic analysis of alkali treated monosaccharides are compiled in *Table 3*. It can be seen that glucose,

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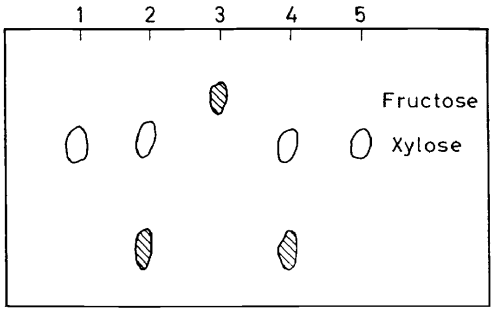

Figure 7. Chromatogram, elution time 6 h [1, Xylose; 2, Hot-alkali-treated xylose; 3, Fructose; 4, Hot-alkali-treated xylose; 5, Xylose]

mannose, and galactose are partly converted into other aldohexoses and into a keto sugar, evidently fructose. Glucose is found in the chromatogram of alkali treated fructose, and mannose and galactose in alkali treated sorbose. In both these cases, there appears weak spots characteristic of arabinose and xylose.

Table 3. Influence of alkali treatment (0·25 N sodium hydroxide at 95°C for 2 h) on monosaccharides

	Sugars identified by paper chromatography after alkali treatment							
	Gal	Glu	Ma	Ar	Xyl	Fru	Sorb	Unident.
Galactose	++		+	(+)	(+)	+		+
Glucose		++	+			(+)		
Mannose		+	++			+		
Xylose				(+)	++			+
Fructose		+		(+)	(+)	++		
Sorbose	+		+	(+)	(+)		++	

++ Abundant + Distinct (+) Very Little

On examining these results from the point of view of pulp making, it seems reasonable to conclude that the substances in acetate grade pulp, which give rise to discoloration during acetylation, are carbohydrates containing keto groups. However, it is unlikely that thoroughly washed pulp contains notable amounts of low-molecular weight sugars. To study if a fructose unit, formed by epimerization from a glucose unit, could remain bound to a cellulose chain, cellobiose was subjected to hot alkali treatment, and subsequently analysed chromatographically. The result is shown in *Figure 8*. As can be seen, glucose and fructose are found. The spot of cellobiose has lengthened and is now of two different colours; the upper part has the blue colour of aldoses (cellobiose) and the lower part the characteristic colour of ketoses. The line 3 corresponds to a sample of alkali treated cellobiose to which saccharose was added before elution. It shows that the keto sugar formed from cellobiose is not saccharose. This can be seen more clearly in the chromatogram (*Figure 9*), which was developed

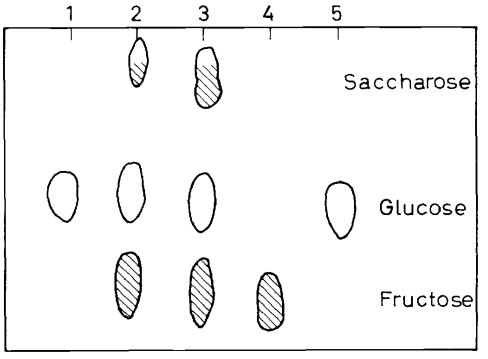

Figure 8. Chromatogram, elution time 24 h [1, Glucose; 2, Hot-alkali-treated cellobiose; 3, Saccharose and hot-alkali-treated cellobiose; 4, Fructose; 5, Glucose]

after a longer elution time. In this case, all three disaccharides are represented by separate spots. Thus, it is justifiable to conclude that the reducing unit of cellobiose was converted to a fructose unit. Similarly, the reducing end unit of a cellulose chain, but possibly also those of different hemicellulose chains may become converted into keto form, without being split off the chain.

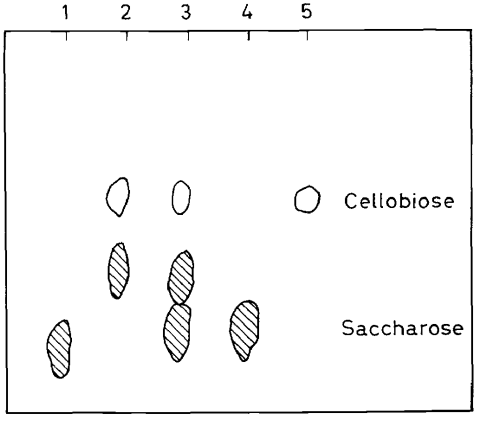

Figure 9. Chromatogram, elution time 120 h [1, Saccharose; 2, Hot-alkali-treated cellobiose; 3, Saccharose and hot-alkali-treated cellobiose; 4, Saccharose; 5, Cellobiose]

One would expect that in the molecule chain of cellulose or hemicelluloses a chain unit containing a keto group could be easily identified by total hydrolysis and paper chromatography. However, fructose units, in general, have not been found in dissolving pulps. The explanation for this is quite simple; fructose does not resist the conditions employed in the total hydrolysis of polysaccharides to the monomer stage. To prove that this is the case, fructose was added to the pulp prior to the hydrolysis. In the chromatogram, no spot of fructose was found, which shows that fructose was either decomposed or converted into other sugars during the hydrolysis.

SUMMARY

Colour development on acetylation of cellulose was studied in model experiments made with low-molecular carbohydrates as test substances. Discoloration was found to occur only when the test substance contained an available keto group. Aldoses, gluconic acid, glucuronic acid and sugar alcohols did not result in the appearance of any colour during acetylation.

It was demonstrated by means of paper chromatographic analysis that during hot alkaline treatment, under conditions such as those employed in conjunction with the bleaching of pulp, glucose, mannose, galactose, xylose and cellobiose were in part converted into keto compounds.

On the whole, the results obtained indicate that compounds containing keto groups and derived from different polysacharides in wood pulp give rise to the discoloration during acetylation.