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CARBOHYDRATE REACTIONS DURING TREATMENT OF KRAFT PULP AND COTTON WITH ALKALINE PEROXIDE

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ABSTRACT

Kraft pulp and alkali-cooked cotton have been treated with hydrogen peroxide in the presence of alkali. The alditol (produced by reduction) and acid end-groups were isolated by chromatography. It is concluded that existing deoxy-aldonic acid end-groups are partly destroyed and new reducing end-groups are produced, which, in turn, are degraded stepwise until the glycosidic bond is reached. Further degradation is then retarded. The presence of hexonic acid end-groups and *C*-(2,3-dihydroxypropyl)tartronic acid in the spent liquor obtained after treatment of hydrocellulose indicate that carbonyl groups have been introduced oxidatively.

INTRODUCTION

The utilisation of H_2O_2 in the pulp and paper industry has increased steadily[1] and it is important to obtain a better understanding of the carbohydrate reactions during the bleaching process and to determine the constitution of H_2O_2-bleached material.

Many experiments have been carried out to elucidate the reactions between alkaline peroxide and carbohydrates at low [2,4] and elevated temperature[5,6]. However, the end-groups present in the solid phase after treatment with H_2O_2–alkali have not been analysed hitherto and this is now reported for kraft pulp, alkali-cooked cotton, and hydrocellulose.

EXPERIMENTAL

Alkali-cooked cotton. — Unbleached cotton was purified by solvent extraction and kier boiling[7], and then treated under nitrogen in 1.25M sodium hydroxide at 170° for 6 h. The cotton was rinsed with water, soaked in 0.2M acetic acid for 30 min, rinsed with water, and dried in circulating air at 32°. This washing procedure was used for all alkali- and peroxide–alkali-treated samples. The intrinsic viscosity of the alkali-cooked cotton was 192 cm^3/g.

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Kraft pulp. — The kraft pulp was made from Scots pine and had an intrinsic viscosity of 1058 cm³/g. The kraft cooking was performed in a rotating autoclave at a wood-to-liquor ratio of 1:4. The composition of the liquor corresponded to 0.06M Na_2S + 0.36M NaOH. The cooking was interrupted by cooling the autoclaves with tap water.

Hydrocellulose. — Unbleached purified cotton (see above) was treated with boiling 0.05M sulfuric acid for 4.5 h at a cotton-to-liquid ratio of 1:25. The hydrocellulose was then treated for 4 min with 1.5M sodium hydroxide at 2°. The intrinsic viscosity was 174 cm³/g.

Alkaline peroxide treatment. — The cellulosic sample (25 g) was suspended in a solution (1 L) which was M with respect to sodium hydroxide and 1.1M with respect to hydrogen peroxide (1.8M for kraft pulp). Freshly boiled water was used.

The sample was pressed until the dry content was 15% (w/w) and then placed in a polyethylene bag, which was filled with nitrogen, sealed, and kept at 65° for 4 h. The sample was then washed. For hydrocellulose, the initial water washings and the spent liquor were retained.

Analysis. — The untreated and the H_2O_2–alkali-treated samples (~16 g) were hydrolysed with hydrochloric acid[8]. The carboxylic acid end-groups were then determined by a combination of anion-exchange chromatography[8] and g.l.c.[9]. This method was also used to determine the soluble, non-volatile monocarboxylic acids obtained by H_2O_2–alkali treatment of hydrocellulose. The corresponding dicarboxylic acids in the latter experiment were separated by anion-exchange chromatography, using 0.3M sodium acetate in 2M acetic acid as eluent[10]. Formic acid was also determined[11] in the spent liquor.

Reducing sugar end-groups of four samples were determined by partition chromatography of the alditols formed after reduction of the sample with potassium borohydride followed by acid hydrolysis[12]. Viscosities were determined on solutions in copper ethylenediamine[13].

RESULTS AND DISCUSSION

The results obtained from experiments on kraft pulp, at first glance, seem to be complicated (Table I). Pulp contains not only cellulose and glucomannan but also xylan. In order to simplify the situation, purified cotton was also subjected to treatment with H_2O_2–alkali. Kraft pulp is virtually free from reducing end-groups, and therefore the cotton was first alkali-cooked, thereby converting the reducing end-groups into carboxylic acid end-groups of the same types as in the cellulose and glucomannan components.

The end groups in untreated alkali-cooked cotton (Table I) are dominated by the so-called stopping acids, namely, 3-deoxyhexonic acids[14] and 2-*C*-methylglyceric acid[15]. It has been reported that no reducing sugar end-groups are present after severe alkali-cooking[15].

After the H_2O_2–alkali treatment, large amounts of reducing end-groups were

TABLE I

NON-VOLATILE ORGANIC ACIDS AND ALDITOLS ISOLATED FROM HYDROLYSATES OF VARIOUS CELLULOSE PREPARATIONS

End group (acids and alditols)	*Kraft pulp*		*Alkali-cooked cotton*		*Hydrocellulose*	
	Untreated *1*	*H_2O_2-treated* *2*	*Untreated* *3*	*H_2O_2-treated* *4*	*Untreated* *5*	*H_2O_2-treated* *6*
3-Deoxy-*ribo*-hexonic	115[a]	56	449	232	[b]	18
3-Deoxy-*arabino*-hexonic	109	34	498	168	[b]	14
2-*C*-Methylglyceric	135	101	452	368	[b]	[b]
3-Deoxy-*erythro*-pentonic	20	[b]	[b]	[b]	[b]	[b]
3-Deoxy-*threo*-pentonic	35	[b]	[b]	[b]	[b]	[b]
Gluconic	28	39	29	46	33	221
Mannonic	27	77	[b]	21	[b]	213
Arabinonic	[b]	[b]	[b]	[b]	22	12
Xylonic	10	25	[b]	[b]	[b]	[b]
Lyxonic	[b]	tr[f]	[b]	[b]	[b]	[b]
Erythronic	27	133	27	395	70	565
Threonic	13	50				
Glyceric	50	223	[b]	[b]	65	[b]
Glucitol[d]	[c]	28	[c]	41	2896	579
Mannitol[d]	[c]	68	[c]	57	15	135
Arabinitol[d]	[c]	[c]	[c]	23	[c]	118
Xylitol[d]	[c]	26	[c]	[c]	tr[f]	[c]
Tetritol[d]	[c]	50[e]	[c]	198[e]	[c]	368[e]
Glycerol[d]	[c]	20	[c]	[c]	[c]	[c]
Total	569	930	1455	1549	3101	2243

[a] From a 100-g sample expressed as μmol. [b] Not detected. [c] Not determined. [d] Originating from the corresponding carbonyl end-groups. [e] Mainly erythritol. [f] Trace.

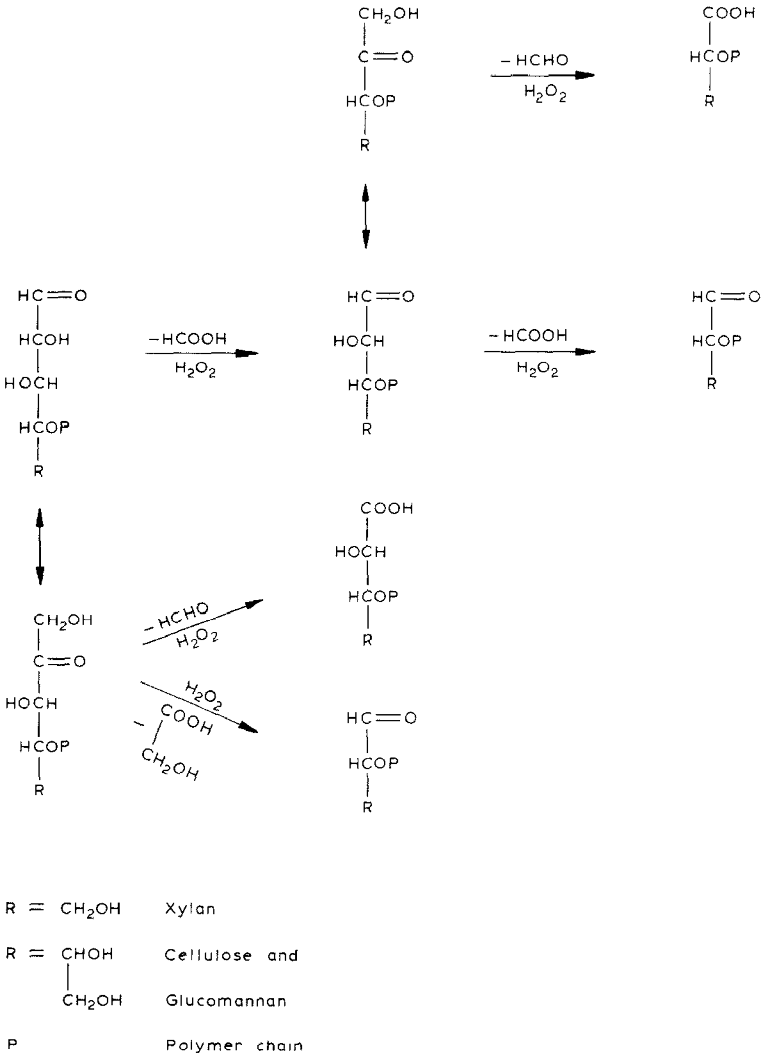
present among which tetroses preponderated (see column 4, Table I), but hexoses and a pentose were also present. The presence of hexose end-groups indicated that new reducing end-groups had been continuously exposed. The acid end-groups present before the treatment with H_2O_2–alkali were also the most abundant group afterwards, but a large amount of tetronic acid end-groups was also present.

For aldoses at low temperature, one molecule of formic acid and one molecule of the next lower aldose are formed on treatment with H_2O_2–alkali[2], and fructose gives either formaldehyde and arabinonic acid or glycolic acid and erythrose[3]. When glycosidically linked, the sugars are rapidly degraded stepwise until the glycosidic bond is reached and then the degradation is retarded[4]. In hot alkaline solution, aldoses are isomerised to the corresponding ketose and epimeric aldose as demonstrated by the presence of mannitol end-groups.

The presence of large amounts of hexonic acid end-groups after the treatment with H_2O_2 indicates that 2-hexosulose end-groups were present. This end group undergoes a benzilic acid-type rearrangement in alkaline medium to give the two hexonic acids[16]. The presence of oxygen (liberated during the peroxide reaction) would be expected to lead to the formation of such α-dicarbonyl compounds[17].

By analogy, the conclusions drawn for the action of alkaline H_2O_2 on alkali-cooked cotton should also be applicable to the cellulose and glucomannan present in the treated kraft pulp (Table I). The products from H_2O_2–alkali-treated, alkali-cooked cotton also are found in column 2 with one exception; arabinose end-groups could not be detected in kraft pulp.

The other end-groups in column 2 in Table I represent the xylan part of treated kraft pulp. It is reasonable to assume that the reactions occurring in cellulose also occur in xylan. For example, the tetronic acid end-groups in treated cotton correspond to glyceric acid end-groups in xylan. The analogy is further demonstrated in Scheme 1, which is based on Isbell's model experiments[2,3]. The



Scheme 1. Schematic representation of the formation of lower aldose and aldonic acid end-groups in a reducing end-group glycosidically linked at C-4.

TABLE II

ORGANIC ACIDS ISOLATED FROM THE SPENT LIQUOR AFTER TREATMENT OF HYDROCELLULOSE WITH H_2O_2–ALKALI

Acid	*μmol*
3-Deoxy-2-*C*-hydroxymethyl-*erythro*-pentonic	622[a]
3-Deoxy-2-*C*-hydroxymethyl-*threo*-pentonic	1639
3-Deoxy-*erythro*-pentonic	460
3-Deoxy-*threo*-pentonic	693
2-Deoxytetronic	6758
Glyceric	1094
Glycolic	8420
Formic	17130
C-(2,3-Dihydroxypropyl)tartronic	1620
Oxalic	1760
Total	40196

[a] From 100 g of hydrocellulose.

reaction pathways explain the formation of all end-groups formed during the treatment with H_2O_2–alkali, except for those containing six carbon atoms from cellulose and glucomannan and five carbon atoms from xylan (see above).

The H_2O_2–alkali treatment of pulp increases the amount of end groups (Table I), the greatest increase (~3-fold) being associated with the xylan. This may be due to chain cleavage caused by oxygen liberated during the peroxide reactions[18] and, for alkali-treated xylan, a type of end group which is not detected by the analytical methods applied[19]. Apparently, during the H_2O_2–alkali treatment, these end groups are destroyed and replaced by others which are detectable. The end groups in kraft pulp were not analysed, because it has been reported that severely alkali-cooked cotton[15] and xylan[19] contain only traces of reducing sugar end-groups.

In order to gain a better understanding of the reactions of aldose end-groups exposed during the treatment, hydrocellulose was also subjected to treatment with H_2O_2–alkali and the end groups were analysed. Columns 5 and 6 in Table I show that the products formed support the reactions proposed above for alkali-cooked cotton and kraft pulp. However, arabinose end-groups were present in quite a large amount, further indicating the formation of new reducing end-groups.

The spent liquor after treatment of hydrocellulose with H_2O_2 was analysed for soluble acids (Table II). The composition resembles that in the spent liquor from O_2–alkali treatment of hydrocellulose. The reducing end-groups are destroyed by the so called "peeling" reactions, producing dicarbonyl compounds, which either undergo benzilic acid rearrangement or are split by the peroxide into two carboxylic acids[20].

The presence of *C*-(2,3-dihydroxypropyl)tartronic acid demonstrates that carbonyl groups have been introduced by oxidation (ref. 10), and further supports the conclusion noted above that the liberated oxygen is important.

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