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THE FORMATION OF END GROUPS IN CELLULOSE DURING ALKALI COOKING

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ABSTRACT

Cotton that had been subjected to alkali cooking at 170° was hydrolysed to determine the carboxylic acid end-groups. Large proportions of 3-deoxy-*ribo*-hexonic, 3-deoxy-*arabino*-hexonic, and 2-*C*-methylglyceric acids, together with a minor proportion of 2-*C*-methylribonic acid, were isolated and identified. Reduction of the cellulose end-groups and subsequent analysis of the hydrolysate revealed 3-deoxy-*ribo*-hexitol, 3-deoxy-*arabino*-hexitol, 2-*C*-methylglycerol, and a small proportion of 2-*C*-methylribitol. It is concluded from these results that, in addition to 3-deoxyhexonic acid end-groups, significant quantities of terminal 2-*C*-methylglyceric and minor amounts of 2-*C*-methylribonic acid groups are formed during the alkali cooking. No alditol end-groups were detected in the unreduced cellulose.

INTRODUCTION

Although the manufacture of kraft pulp is an important industrial process, the cellulose reactions occurring during the cooking of kraft pulp are incompletely understood. The presence of 3-deoxy-*ribo*- and 3-deoxy-*arabino*-hexonic acid end-groups has been demonstrated qualitatively by various chromatographic methods[1,2], but quantitative determination has not been attempted. We now report methods for the study of the formation of end groups under conditions simulating the cooking of kraft pulp.

EXPERIMENTAL AND RESULTS

Alkaline treatment of cotton and subsequent hydrolysis with acid. — Unbleached cotton (170 g), purified by solvent extraction, kier boiling[3], and extraction in 6% aqueous sodium hydroxide at 2° for 2 min, was introduced into an autoclave (10 l) containing 8.5 l of 5% aqueous sodium hydroxide through which nitrogen had been bubbled for 30 min. The autoclave was evacuated and the temperature raised to 170° during 3 h in the following manner: at 40° and 80° the autoclave was evacuated, and at 120° it was vented. After a cooking-time at 170 ±3° of 7 h, the autoclave was

cooled, and the liquor was filtered off. The cotton was then washed with water, soaked for 1 h in 1% acetic acid, washed with water again, and dried in circulating air at 30°. The yield was 73.5%, and the intrinsic viscosity in copper ethylenediamine[4] was 148 cm^3/g.

The cellulose (130 g) was placed in a glass vessel (2 l) and cooled to −22°, and hydrochloric acid (1.8 l, 43%) at the same temperature was added. The vessel was sealed, kept at 23° for 10 h, and again cooled to −22°, at which the gas was vented. The hydrochloric acid was largely removed by evaporation at 35°. To decompose the reversion products, the residue was diluted with water to a hydrochloric acid concentration of 0.35M and kept at ~90° for 23 h.

The hydrolysate was stirred with Dowex-1 x8 (HCO_3^-) resin (50–100 mesh; 750 ml) for 16 h to remove chloride ions, as well as organic acids and lactones. The resin slurry was transferred to a column and washed with water until the effluent gave a negative anthrone test. The effluent containing the sugars was concentrated *in vacuo* and analysed by partition chromatography[5]. The resin was transferred to a beaker, and 5M acetic acid was added to liberate carbon dioxide. This slurry was poured into a column which contained a short bed of Dowex-1 x8 (AcO^-) resin. The monocarboxylic acids were eluted with 0.2M sodium acetate (15 l). The cations were exchanged for hydrogen, and the eluate was evaporated to dryness to give a residue of 763 mg.

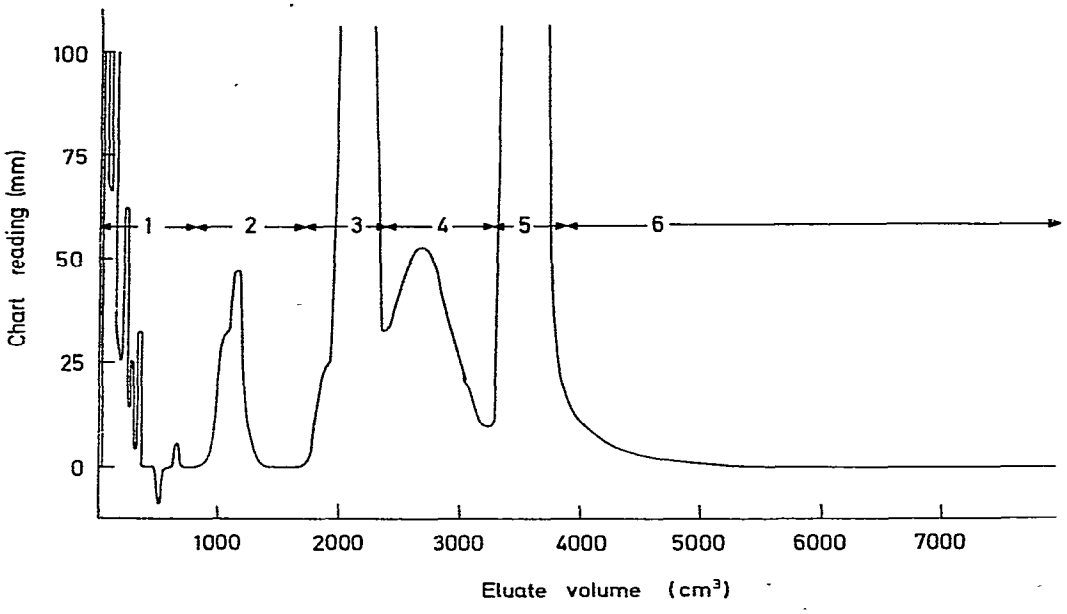

Fig. 1. Group separation of monocarboxylic acids isolated after hydrolysis of cotton cellulose that had been cooked with hot alkali. Eluent: 0.08M sodium acetate (pH 5.9). Column (20 × 800 mm): Dowex-1 x8, 25–32 μm. Nominal flow: 0.8 $cm.min^{-1}$. Analysis by Waters R 401 differential refractometer.

Separation and identification of acids. — The non-volatile, organic acids were separated into groups by anion-exchange chromatography[6], and bands were cut as indicated in Fig. 1. After removal of sodium ions, the fractions were evaporated to dryness and weighed.

The position of band 3 (the first major fraction) suggested that it contained 3-deoxy-*ribo*- and 3-deoxy-*arabino*-hexonic acids. This was substantiated by pre-

TABLE I

DISTRIBUTION COEFFICIENTS (D_v) IN ACETIC ACID AND SODIUM ACETATE MEDIA, AND COLOUR RESPONSES IN CHROMIC ACID (Cr), PERIODATE–FORMALDEHYDE (P–f), AND CARBAZOLE (K) CHANNELS

Band number	*mg/130 g*	*Acids*	D_v *in ion-exchange chromatography*		*Colour response*[a]		
			0.08M NaOAc	*0.5M HOAc*	*Cr*	*P–f*	*K*
3:S1	3.4	2-*C*-Methylribonic	6.70	5.53	+	+	−
3:S2	86	3-Deoxy-*ribo*-hexonic	7.12	6.85	+	+	(+)
3:S3	82	3-Deoxy-*arabino*-hexonic	7.64	9.50	+	+	(+)
3:S4	7.1	Unknown 1	6.54	24.3	+	+	(+)
4:S1	13	3-Deoxy-*ribo*-hexonic levulinate	6.65[b]	5.89	+	+	(+)
4:S2	10	3-Deoxy-*ribo*-hexonic	7.20	6.80	+	+	(+)
4:S3	24	3-Deoxy-*arabino*-hexonic levulinate	9.08	8.43	+	−	(+)
4:S4	10	3-Deoxy-*arabino*-hexonic	7.60	9.67	+	+	(+)
4:S5	6.8	Gluconic	7.21	12.5	+	+	−
4:S6	5.7	Arabinonic	8.93	14.2	+	+	−
	8.2	2-*C*-Methylglyceric	11.1	14.2	+	+	−
4:S7	1.3	Anhydrosaccharinic		17.2			
4:S8	1.4	Mannonic	9.50	17.5	+	+	−
4:S9	7.7	Erythronic	10.5	18.9	+	+	−
4:S10	9.8	Anhydrosaccharinic	10.4	24.2	+	−	+
5:S1	312	Levulinic	12.9	3.25	+	−	−
5:S2	8.8	2-*C*-Methylglyceric levulinate	7.12	12.0	+	+	−
5:S3	45	2-*C*-Methylglyceric	11.1	14.0	+	+	−
5:S4	9.0	Glyceric	12.0	19.8	+	+	−
5:S5	11	2-*C*-Methylglyceric levulinate	13.4	25.6	+	−	−
6:S1	11	Levulinic	13.1	3.50	+	−	−
6:S2	2.7	2-*C*-Methylglyceric	11.1	14.4	+	+	−
6:S3	2.3	Lactic	13.9	15.0	+	−	(+)
6:S4	3.0	Glycolic	14.7	17.8	+	(+)	+
6:S5	12.0	2-*C*-Methylglyceric levulinate	13.4	25.8	+	−	−
6:S6	6.0	Unknown 2	—	38.6			

[a]Key: +, positive reaction; (+), weak reaction; −, no reaction. [b]Two peaks were recorded in the acetate run, one with the values in the Table, and one with $D_v = 8.93$ and colour responses + − (+).

parative rechromatography, using 0.5M acetic acid, and by determinations of the D_v values [Table I] on analytical columns coupled with a three-channel analyzer[7]. Final confirmation was obtained by g.l.c.–m.s. of the trimethylsilyl-substituted trimethylsilyl (TMS) esters[8]. Unless stated otherwise, the acids discussed below were identified by the same methods. In addition to 3-deoxyhexonic acids, band 3 contained a minor amount of 2-*C*-methylribonic acid as well as a small amount of an unknown acid.

Band 4 constituted only a minor part of the organic acids. Due to overlapping, it also contained both the 3-deoxyhexonic acids present in band 3. In addition, gluconic, arabinonic, 2-*C*-methylglyceric, mannonic, and erythronic acids were present in small amounts. An anhydrosaccharinic acid, which is formed as an artefact during acid hydrolysis[9], was obtained together with a minor amount of another acid (4:S7) that gave an almost identical mass spectrum. The results indicated that this acid was the diastereomer. Two of the major peaks obtained when band 4 was rechromatographed in 0.5M acetic acid contained 4-oxovaleric (levulinic)esters of the two 3-deoxyhexonic acids. This fact was established by saponification and identification of the products by the methods described above. The results indicate that these esters, as well as those present in band 5, are formed during the removal of the acetic acid by evaporation.

Similarly, band 5, which contained levulinic acid (artefact) and 2-*C*-methylglyceric acid as the main components, also contained appreciable amounts (see Fig. 2

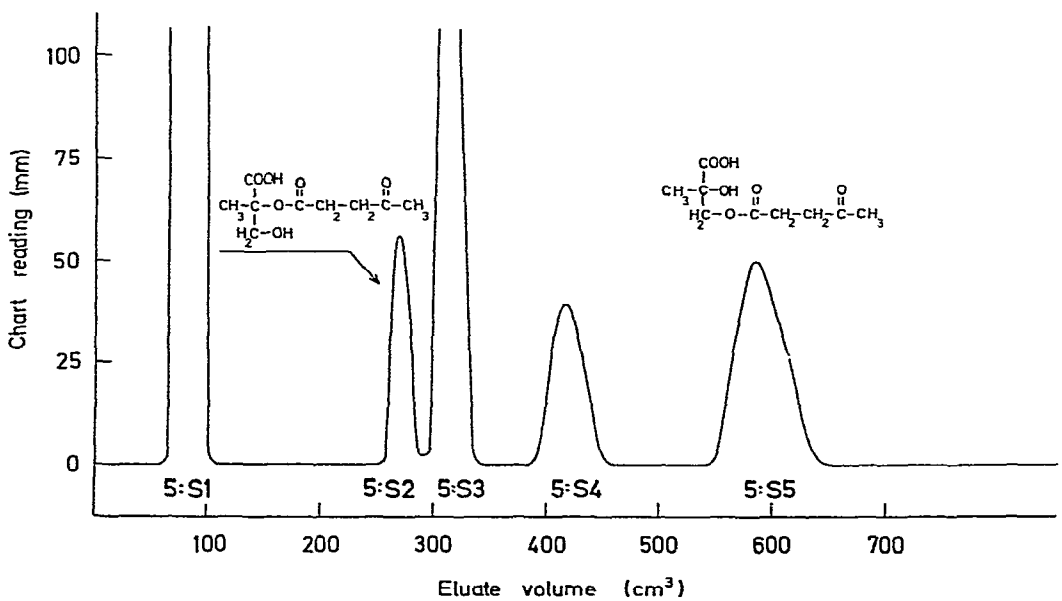

Fig. 2. Separation of monocarboxylic acids from band 5. Eluent: 0.5M acetic acid. Column (6 × 780 mm): Dowex-1 x8, 37–41 μm. Nominal flow: 0.21 cm.min^{-1}. Analysis by Waters R 401 differential refractometer.

and Table I) of two compounds which, after saponification at pH 10 for 4 h at room temperature, gave levulinic and 2-*C*-methylglyceric acids. Evidently, these compounds were esters. The structure of the compound 5:S5 was deduced by g.l.c.–m.s. of the TMS derivative[8] and is shown in Fig. 2. The structure of the ester contained in band 5:S2 is most probably that shown in Fig. 2.

Band 6 contained only minor amounts of acids and, as expected from the tailing of band 5, levulinic acid, 2-*C*-methylglyceric acid, and one of the levulinic esters of 2-*C*-methylglyceric acid were present. As in the corresponding fraction of all other polysaccharide hydrolysates studied in this laboratory, band 6 contained small proportions of lactic and glycolic acids. A minor amount of an unknown acid, which was held strongly during column chromatography in acetic acid was also present.

Bands 1 and 2, which contained only minor amounts of material, had positions corresponding to those of oligomeric acids. Hydrolysis of the material in band 1 in 0.1M sulphuric acid at 130° for 3 h released glucose, the two diastereomeric 3-deoxyhexonic acids (5 mg of each), and 2-*C*-methylglyceric acid (4 mg). Minor amounts of gluconic, arabinonic, erythronic, glyceric, and levulinic (artefact) acids were also detected.

Rechromatography of band 2 in 0.5M acetic acid showed that it contained at least six different organic acids with positions similar to those recorded for aldobionic acids. After hydrolysis, glucose and appreciable amounts of the two 3-deoxyhexonic and 2-*C*-methylglyceric acids were obtained. These results strongly indicate that the acids contained in bands 1 and 2 are mainly reversion products. The amounts of acids found in the hydrolysates from bands 1 and 2, as well as the amounts of acids recovered after saponification of the levulinic esters, are added to the amounts of the acids reported in Table II.

TABLE II

SACCHARINIC AND ALDONIC ACIDS IN THE HYDROLYSATE

Acids	*Weight (mg)*[a]
3-Deoxy-*ribo*-hexonic	100
3-Deoxy-*arabino*-hexonic	105
2-*C*-Methylribonic	3.4
2-*C*-Methylglyceric	64
Gluconic	5.3
Mannonic	1.1
Arabinonic	4.4
Erythronic	5.9

[a]Calculated on 100 g of alkali-cooked cotton.

Furthermore, trace amounts (probably artefacts) of 3-deoxy-2-*C*-(hydroxymethyl)pentonic acids (*erythro* and *threo*) were present in band 3 and in the hydrolysate of band 1.

The results in Table II confirm the previous findings that the formation of terminal 3-deoxyhexonic acid groups is an important reaction occurring during the alkali-cooking at high temperatures[1], and that these groups are the most abundant, acidic end-groups. Moreover, the results strongly indicate that, in addition, a large number of 2-*C*-methylglyceric acid end-groups are formed. The small amount of 2-*C*-methylribonic acid isolated from the hydrolysate can also be attributed to terminal groups formed during the cooking. The reactions which give rise to these acids will be briefly discussed in the Discussion section.

The small proportions of aldonic acids found in the hydrolysate are derived from aldonic acid end-groups present in the raw cotton[10] and formed by oxidation of cellulose in alkaline medium during purification. These acids will, therefore, not be discussed in detail.

Determinations of monosaccharides and alditols. — The sugar fraction obtained after removal of the organic acids and the hydrochloric acid from the hydrolysate was chromatographed on a cation exchanger in the lithium form (Aminex A6; 10–19 μm; Bio Rad) and also on an anion exchanger in the sulphate form (T5A; 15–20 μm; Technicon), with automatic analysis of the eluate by the orcinol and periodate–formaldehyde methods[5]. In addition to glucose, trace amounts of xylose, and the usual artefacts formed during the hydrolysis (fructose, mannose, arabinose, 1,6-anhydroglucoses, and reversion products) were present. Alditols were not found on the chromatograms; since the method is very sensitive, alditol end-groups must constitute less than 0.0005% of the cellulose.

Determinations of alditols by the same techniques were made on alkali-cooked samples which, before the acid hydrolysis, had been reduced with sodium borohydride. Experiments were carried out on the original sample (dried after soaking in acetic acid before the final washing with water) and on the same sample after pretreatment with an alkaline salt solution to open the lactone rings[11].

In the lactone-containing sample, significant peaks were recorded in the periodate–formaldehyde channel with positions corresponding to 3-deoxy-*ribo*-hexitol (8 mg), 3-deoxy-*arabino*-hexitol (16 mg), and glucitol (10 mg) for the sulphate resin. These and all other amounts of products reported here are calculated per 100 g of dry, alkali-cooked cotton. The presence of glucitol was confirmed by chromatography on the lithium column. The deoxyhexitols appeared together with glucose, and therefore could not be detected with the latter type of resin. The distribution coefficients of the alditols are given in Table III, together with those of xylitol, which served as a marker. The sample subjected to alkaline pretreatment to open the lactones gave a significant peak for glucitol (8 mg). No peaks could be observed at the positions of the 3-deoxyhexitols. The results from this sample show that only a very small fraction of the end groups in the alkali-cooked cotton are reducing glucose end-groups. It is not clear whether any glucose groups are actually present at the end of the alkali-cooking, since it is possible that a small proportion of glucosidic bonds were cleaved during subsequent treatments, which then gave rise to the glucitol end-groups subsequently detected.

TABLE III

VOLUME DISTRIBUTION COEFFICIENTS OF SOME ALDITOLS AT 75° AND 85% ETHANOL

Alditol[a]	*Li^+ resin*	*SO_4^{2-} resin*
3-Deoxy-*ribo*-hexitol	2.51	3.13
3-Deoxy-*arabino*-hexitol	2.68	3.78
2-*C*-Methylribitol	1.30	2.53
2-*C*-Methylarabinitol	1.39	2.15
2-*C*-Methylglycerol	0.65	0.78
Xylitol	4.21	5.34

[a]The four first alditols were prepared by reduction with sodium borohydride of the lactones of the corresponding saccharinic acids. 2-*C*-Methylarabinonic acid was kindly supplied by Professor O. Theander. 2-*C*-Methylglyceric acid was reduced with lithium aluminium hydride, and the structure of the alditol confirmed by g.l.c.–m.s. of its TMS derivative.

The higher value of glucitol obtained with the lactone-containing sample may be ascribed to reduction of terminal gluconolactone units. The presence of 3-deoxy-*ribo*- and 3-deoxy-*arabino*-hexitols confirms that the 3-deoxyhexonic acids found in the hydrolysate are present as end groups and shows that they have the ability to form ester linkages (probably 1,5-lactones). The amount of alditols was much less than the amount of 3-deoxyhexonic acids isolated from the hydrolysate. This finding indicates that the formation of esters is not extensive.

To increase the yield of alditols, the reduction was carried out with lithium aluminium hydride for 14 days at room temperature in tetrahydrofuran with ultrasonic treatment. Before adding the solvent, the alkali-cooked sample was treated in succession with methanol, ethyl ether, and tetrahydrofuran. Determinations of alditols by the same chromatographic methods gave the results presented in Table IV. As expected, large quantities of 3-deoxy-*ribo*-hexitol and 3-deoxy-*arabino*-hexitol

TABLE IV

AMOUNTS OF ALDITOLS[a] RECORDED IN HYDROLYSATES AFTER REDUCTION WITH LITHIUM ALUMINIUM HYDRIDE

Alditols	*Li^+ resin*	*SO_4^{2-} resin*
3-Deoxy-*ribo*-hexitol		28
3-Deoxy-*arabino*-hexitol		29
2-*C*-Methylribitol		1.4
2-*C*-Methylglycerol	21	
Glucitol	68	70
Mannitol	1.9	1.9
Arabinitol	2.9	2.6
Erythritol[b]	8.5	

[a]Mg/100 g of alkali-cooked cotton. [b]Erythritol has the same position as 3-deoxy-*ribo*-hexitol on the sulphate resin. The amount of 3-deoxy-*ribo*-hexitol is therefore corrected for the amount of erythritol recorded in the run on the lithium resin.

were obtained, but the amounts were only about 25% of those expected for a quantitative reduction of the 3-deoxyhexonic acid end-groups. The results clearly show that the reduction was incomplete, probably as a result of low accessibility of the terminal groups.

A striking confirmation of the conclusion that 2-*C*-methylglyceric acid end-groups are responsible for the presence of this acid in the hydrolysate followed from the fact that 2-*C*-methylglycerol was one of the more abundant terminal groups in the reduced sample. The absence of this alditol, following reduction with sodium borohydride after lactonisation, is explained by the inability of the corresponding acid end-groups to give lactones.

A small, but unfortunately overlapping, peak with the position of 2-*C*-methylribitol indicates that the 2-*C*-methylribonic acid found in the hydrolysate was derived from terminal units. The overlapping compound was not identified.

Since aldonic acid end-groups were detected, the presence of small amounts of glucitol, mannitol, arabinitol, and erythritol was expected. The results in Table IV show, however, that the amount of glucitol detected was considerably larger than the sum of the gluconic acid end-groups (Table II) and the maximum amount of glucose end-groups estimated after reduction with borohydride. This finding indicates that some glucosidic bonds must have been cleaved during the treatment with lithium aluminium hydride.

Stability of the saccharinic acids towards acid hydrolysis and alkali-cooking. — In separate experiments, samples of 2-*C*-methylglyceric, 2-*C*-methylribonic, 3-deoxy-*ribo*-hexonic, and 3-deoxy-*arabino*-hexonic acids (~10 mg) were subjected to the treatment with hydrochloric acid used for the hydrolysis of cotton. After evaporation, the organic acids and chloride ions were adsorbed on an anion exchanger in its hydrogencarbonate form, as described above. The organic acids were eluted with 5M acetic acid, and the eluates were evaporated to dryness and weighed. In none of the experiments was the loss in weight (including that due to lactone formation) larger than 8%. Samples of the recovered acid were chromatographed on analytical columns, using sodium acetate and acetic acid as described above. From the D_v values and the colour responses (compared with those of authentic samples), no degradation effects were detected. For further confirmation, the sodium salts of the acids were converted into TMS derivatives; their g.l.c. behaviour was identical with that of the authentic samples.

Similar experiments were made with alkali treatment (5% sodium hydroxide) at 170° for 7 h. After removal of the alkali with a cation-exchange resin, the same methods, including the treatment with anion-exchange resin, were applied to check possible degradation and rearrangements. The recovery of 2-*C*-methylribonic and 2-*C*-methylglyceric acids was ~98%, and no traces of new products could be detected.

In agreement with the earlier observation[12], it was found that the *ribo* and *arabino* forms of the 3-deoxyhexonic acids were interconverted. In the experiment with the *ribo* form, the ratio between areas of the peaks corresponding to the *arabino*

and *ribo* forms was 1.09, whereas in the run with the *arabino* form the ratio was 1.26. The results show that equilibrium was not attained within 7 h. No degradation products were recorded, and the total yield was at least 95%.

DISCUSSION

The degradation of the cellulose molecule during alkali-cooking at high temperature starts by a cleavage of D-glucosidic bonds along the molecular chain. Terminal D-glucose end-groups are formed and these end groups are then attacked[13] by a stepwise degradation ("peeling") of the same type as that occurring during the treatment of hydrocellulose with alkali at lower temperatures[14].

The formation of carboxylic acid end-groups renders the terminal group almost stable towards further attack[14,15] and, as shown by Machell and Richards[14], the formation of 3-deoxyhexonic acid end-groups explains the stopping of the peeling reaction during treatment of hydrocellulose with alkali. As already mentioned, the same stopping-reaction occurs during alkali-cooking[1] and during kraft-pulp cooking of wood[2,16]. No attempt to determine quantitatively the terminal acid groups formed during alkali cooking has been made previously. The results in Table II show that large proportions of the 3-deoxyhexonic acids are present in the hydrolysate. The determinations of the alditols, referred to above, confirm that these acids are derived from the terminal groups. Hence, additional support is obtained for the importance of this type of stopping reaction.

The possible formation of the 2-*C*-methylribonic acid end-group has been discussed by Machell and Richards[14], who tentatively identified it by paper chromatography in a hydrolysate of cotton hydrocellulose that had been treated with alkali at 100°. A minor quantity of this acid was also tentatively identified in an Eucalypt kraft pulp[2]. The results of the present research confirm that terminal 2-*C*-methylribonic acid units are formed under conditions simulating kraft-pulp cooking, but that the reaction path which gives rise to this terminal unit is of minor importance.

A more important reaction is the formation of 2-*C*-methylglyceric acid end-groups. This reaction has not been observed by earlier investigators. 2-*C*-Methylglyceric acid has previously been detected in hydrolysates from unbleached Eucalypt and pine pulps[2]. No attempts were made, however, to determine whether this acid is derived from end groups or from impurities, or is simply an artefact. The results given here show that this acid is derived from the end groups in the cellulose molecules, and hence that terminal, 2-*C*-methylglyceric acid end-groups are present in commercial pulps. The formation of 2-*C*-methylglyceric acid end-groups may be initiated by Lobry de Bruyn–Alberda van Ekenstein rearrangements of a D-glucose end-group, which give rise to terminal moieties having a keto group at C-3 (see Fig. 3). This terminal unit is then subject to a reverse aldol reaction, which leads to a splitting off of glycolaldehyde and the formation of an end group which then gives rise to elimination of the β-hydroxyl group at C-1 accompanied by the formation of an unstable dicarbonyl moiety. By a benzilic acid type rearrangement, this group is

converted to a terminal 2-*C*-methylglyceric acid group. The isolated acid exhibited no detectable optical rotation, which shows that, as expected, both D and L forms were formed.

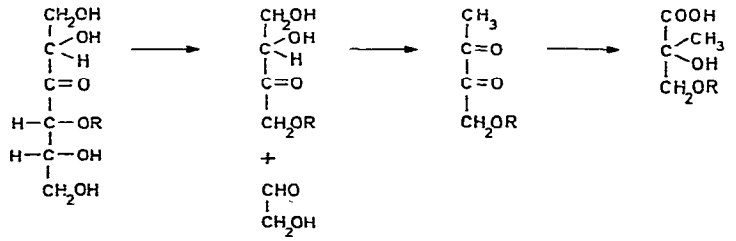

Fig. 3. Proposed route for the formation of 2-C-methylglyceric acid end-groups during alkali cooking of cotton cellulose.

When 3-deoxyhexonic, 2-*C*-methylribonic, and 2-*C*-methylglyceric acids were treated with alkali, no degradation could be detected after 7 h at 170°. The 3-deoxyhexonic acids were, however, slowly interconverted by epimerization, but the acids lacking an acidic hydrogen at C-2 were unchanged.

The total number of carboxylic acid end-groups in the alkali-cooked sample, as determined by alkalimetric titration[11], was 2.31 mmoles per 100 g. The total amount of 3-deoxyhexonic acids recovered in the hydrolysate was 1.14 mmoles per 100 g, *i.e.*, 49% of the carboxyl number. The amount of 2-*C*-methylribonic acid corresponds to 1%, and that of 2-*C*-methylglyceric acid to 23% of the carboxyl number. The sum of the aldonic acids listed in Table II is equal to 0.11 mmole, which corresponds to 5%. Hence, 78% of the carboxylic acid end-groups were accounted for by these determinations. The losses of acids during the hydrolysis and removal of mineral acid are very small. On the other hand, losses cannot be avoided during chromatography. It can therefore be concluded that, in addition to the carboxylic acid end-groups discussed above, only minor amounts of other acid end-groups can be present after the alkali-cooking.

From molecular weight determinations by osmosis, and from determinations of the total number of carboxylic acid groups in alkali-cooked cotton, Franzon and Samuelson[15] concluded that ~70% of the cellulose molecules contained a carboxylic acid end-group. Since D-glucose end-groups were virtually absent, some other, non-ionic, terminal unit must be present. It has been suggested that arabinitol and erythritol end-groups are formed by cleavage of formic and glycolic acids, respectively, from the terminal D-glucose residue[17]. The possibility of the formation of D-glucitol end-groups has also been reported[14]. These hypotheses are disproved by the observation that no alditol end-groups are present in the alkali-cooked sample. The alditol determinations were repeated with another sample of alkali-cooked cotton and again no traces were recorded.

The results of the present work do not permit further conclusions about the non-ionic, terminal units, except that they confirm that D-glucose end-groups, and other reducing sugar moieties, are virtually absent. From model experiments with cellobiitol, Dryselius, Lindberg, and Theander[18] concluded that terminal 1,6-anhydro-D-glucose residues are formed during the alkali digestion, but, unfortunately, analytical techniques are not available for the direct determination of these groups in the cellulose.

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