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Studies on Mechanically Degraded Cellulose

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Mechanically degraded cellulose was investigated by reduction with borohydride, hydrolysis and isolation of the glycitols in the hydrolysate. The major component was D-glucitol, but D-arabitol, erythritol and traces of glycerol were also found. These results show that carbon-carbon as well as carbon-oxygen linkages are ruptured and thus strongly indicate that the degradation is entirely a mechanical effect.

Mechanical treatment of cellulose by grinding in a ball mill and in other ways produces severe degradation. Previous studies, which have been summarised by McBurney [1], have shown that the DP is decreased during milling. The carboxyl content increases only slightly, and it has been definitely proved that the degradation is not due to oxidation by atmospheric oxygen. As the degradation is rather independent of temperature, a hydrolytic mechanism has also been considered less likely. The most probable explanation is that the degradation is entirely mechanical. Hess and Steurer [2] have shown that the kinetic energy available from the impact of the balls on the cellulose fibre should be sufficient if converted directly to molecular vibrational energy to rupture covalent bonds. The energy requirements for the rupture of carbon-carbon and carbon-oxygen bonds are of the same order, 80—90 kcal., and it could be expected that both types would be broken. The present paper describes a study of the linkages broken when cellulose is ground in a ball mill.

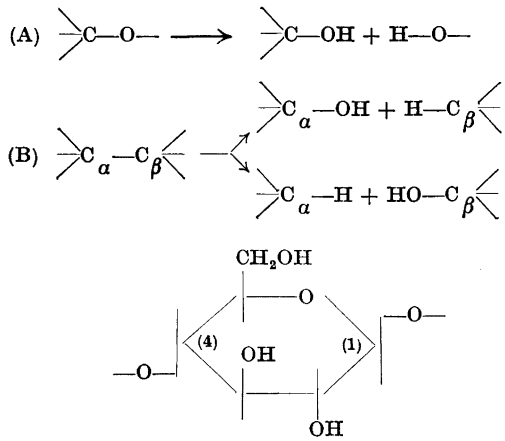
Cotton cellulose was ground in an agate ball mill and the copper number was determined at intervals (according to Hägglund). It rose from 0.2 to 6.5 in five days. A sample treated for 4 days was subjected to chemical investigation. A carbonyl determination by the borohydride method [3] indicated 2.7 carbonyl-groups per 100 glucose residues. According to a recent investigation [4], this value is somewhat too low and the real value should be about 35 % higher. The milled cellulose was treated with borohydride, filtered off and washed. The material that went into solution was recovered (0.5 %). Paper chromatographic investigation of this fraction indicated the presence of glucitol, cellobiitol and higher oligosaccharides together with glycitols with 3, 4 and 5

carbon atoms. The modified cellulose was subjected to a heterogeneous hydrolysis with N sulphuric acid. Most of the reducing sugars and any other aldehydes which might have been present were oxidised to acids by treatment with chlorite at pH 4 and removed by ion exchange. The last traces of sugars were removed by treatment with 0.5 N sodium hydroxide at 100°, followed by ion exchange. The neutral residue (0.6 %) contained components chromatographically indistinguishable from glucitol, arabitol, erythritol and glycerol. Their acetates were indistinguishable from the corresponding authentic acetates on chromatograms on dimethyl sulphoxide-impregnated paper [5], which gives good separation of the fully acetylated glycitols. Fractionation of the neutral mixture gave erythritol, D-arabitol and D-glucitol which were isolated and characterised as crystalline derivatives.

The relative proportions of glucitol, arabitol and erythritol were about 10:3:2, as estimated from the weights of the amorphous, not quite pure fractions obtained. 1,6-Anhydro-D-glucopyranose, which is known to be formed by the acid treatment of glucose [6], was also isolated. In many solvent systems it has the same R_F value as glycerol but the two substances can be separated by elution with butanone, saturated with water; traces of glycerol were detected using this solvent system.

Part of the residue from partial hydrolysis was hydrolysed completely and then worked up as above giving a small amount of neutral material (0.2 %) with the same chromatographic pattern as the material from the heterogeneous hydrolysis.

From these results it is obvious that both C—O and C—C linkages are broken. Rupture of these linkages could be either homolytic or heterolytic. A discussion of this and the subsequent reactions, leading ultimately to stable products, would be highly speculative, but for simplicity it may be assumed that the radicals or ions formed by rupture are stabilised by addition of the elements of water (A and B).



I

If a $C_{(1)}$—O or O—$C_{(4)}$ linkage in a glucose residue (I) of the cellulose molecule is broken, the final result should be equivalent to an acid hydrolysis, possibly accompanied in the second case by some inversion at $C_{(4)}$. Rupture of the linkage between the ring oxygen and either $C_{(1)}$ or $C_{(5)}$ would probably have a similar effect. Reduction and hydrolysis would then yield D-glucitol and possibly D-galactitol.

Rupture of a C—C linkage and subsequent reduction and hydrolysis should yield a glucitol with n carbon atoms together with an aldehyde of (6—n) carbon atoms, which would be removed by oxidation and ion exchange. It is easily seen that the glycitols which could be expected are D-arabitol, erythritol, glycerol and ethylene glycol. The first two were isolated and characterised and indications were found of the presence of glycerol, although in quite small quantities. The presence of ethylene glycol and of any methanol formed as a consequence of $C_{(5)}$—$C_{(6)}$ rupture might easily have been overlooked. D-Glucitol is, however, the major product, indicating that the C—O linkages are somewhat weaker than the C—C linkages. More detailed conclusions cannot be drawn from the results of this investigations, since a high percentage of the oxo-groups in the degraded cellulose is not accounted for and the determination of the relative proportions of the glycitols isolated is at best only semi-quantitative. In addition the course of the reactions leading to stabilisation of the primary products of the rupture of a linkage is quite unknown. As stated already the main result is the strong evidence of an entirely mechanical rupture of covalent linkages by mechanical treatment of cellulose, in agreement with the theory of Steurer and Hess [2].

EXPERIMENTAL

Melting points are corrected. Concentrations were done under reduced pressure at a bath temperature of about 40°.

Paper chromatograms were run on Whatman No. 1 and 3 MM filter papers, using the solvent systems (v/v):

a. Ethyl acetate-acetic acid-water, 3:1:3 (upper phase)
b. Butanone, saturated with water
c. Light petroleum. Paper impregnated with dimethylsulphoxide.

Silver nitrate in acetone-ethanolic sodium hydroxide was used as spray reagent for the detection of glycitols.

Preparation of degraded cellulose. Cellulose (cotton linters) was disintegrated in a Wiley mill and then milled in an agate ball mill for 4 days. During the milling the copper number, determined according to Hägglund [7], increased from 0.21 to 4.62. A borohydride analysis indicated the presence of 2.7 oxo-groups per hundred glucose residues.

Isolation of glycitols from the degraded cellulose. Mechanically degraded cellulose (25.0 g) was suspended in a solution of sodium borohydride (8.0 g) in water (250 ml) for 2 days at room temperature. It was then filtered off and washed with water. The filtrate and washings were concentrated, filtered through a column of Amberlite IR 120 (H^+), concentrated further and boric acid was removed by distillations with anhydrous methanol. A neutral residue (139 mg) was obtained.

This cellulose residue, which had a copper number of 0.37, was refluxed with N sulphuric acid for 4 h and then the undissolved residue (21.3 g) was removed by filtration. The filtrate was neutralised with barium carbonate and concentrated to a syrup (3.8 g). This syrup, dissolved in 0.1 M acetate buffer of pH 3.5, was treated with sodium chlorite (35 g) for 2 days at room temperature. Excess oxidant remaining was reacted with sulphur dioxide and the resultant solution was neutralised with barium carbonate, deionised by filtering through columns of IR 120 (H^+) and IR 4B (free base) and concentrated.

Table 1. Fractionation of the neutral products.

	Directly dissolved		Obtained after partial hydrolysis	
	I	II	I	II
Weight of sample, mg	139	230	150	331
D-Glucitol, mg	12	28	62	95
D-Arabitol, mg	5	10	15	27
Erythritol, mg	6	8	7	22
1,6-Anhydro-D-glucose + Glycerol, mg	Traces	Traces	42	59

The resulting syrup (430 mg) contained glycitols and 1,6-anhydro-D-glucose, together with reducing sugars, glucose, mannose and xylose, as shown by paper chromatography. It was therefore dissolved in 0.5 N sodium hydroxide and kept at 100° for 2 h and then deionised and concentrated, yielding a syrup (150 mg). An analogous experiment, starting from 42 g of degraded cellulose, yielded 230 and 331 mg of neutral material, obtained by direct solution and after partial hydrolysis, respectively.

Part of the residual cellulose (500 mg) was subjected to total hydrolysis in the usual manner and worked up as above, giving a small residue (1.3 mg). Chromatographic investigation showed the presence of 1,6-anhydro-D-glucose (60 %), D-glucitol (30 %) and smaller amounts of D-arabitol and erythritol.

Fractionation of the neutral products. The material that dissolved during the borohydride reduction was fractionated by chromatography on thick filter paper, using solvent a. Only glucitol and the components of higher R_F were recovered. The products obtained after partial hydrolysis were fractionated on a cellulose column, using butanol saturated with water, as eluant. The results of the fractionations are summarised in Table 1.

Characterisation of the components. The components found were chromatographically indistinguishable from authentic samples of D-glucitol, D-arabitol, erythritol, glycerol and 1,6-anhydro-D-glucose respectively, and the same was true for the corresponding acetates.

D-Glucitol was characterised as the hexaacetate, m. p. 99—100°, alone or mixed with an authentic sample.

D-Arabitol was obtained crystalline, m. p. 101—102°, undepressed on admixture with an authentic sample.

Erythritol was characterised as the tetrabenzoate, m. p. 189—191°, alone or mixed with an authentic sample.

1,6-Anhydro-D-glucose was characterised as the tribenzoate, m. p. 201—202°, alone or mixed with an authentic sample.

Glycerol was present in insufficient amount for a definite characterisation.

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