393. *Polysaccharides. Part XXXVI. Hydrocellulose.*

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A specimen of fibrous hydrocellulose was separated mechanically into fibre and powder. Each form gave more than 90% of crystalline glucose on acid hydrolysis. Acidic hydroxyl groups and uronic acid residues were shown to be absent from each form. End-group assay showed that the original hydrocellulose had an average chain length of 120 glucose units and the fibrous portion a chain length of 200 units. The iodine number of the powder form corresponded to a chain length of 70 glucose units.

The solubilities in alkali of fibrous and powder forms of hydrocellulose are compared with the solubilities of linters and of short-chain cellodextrins.

The hydrocellulose used in this investigation had retained the fibrous appearance of the original cotton. It was separable, however, by mechanical teasing into a friable white powder and a fibrous material indistinguishable by eye from cotton linters. The powder had a copper number of 5·4 and was comparable with the hydrocellulose (Cu No. 3·3) described in the preceding paper. The fibrous fraction had Cu No. 1·7 and the original hydrocellulose (the mixture of fibre and powder) had Cu No. 2·6. It is seen that the reducing power even of the fibre is much greater than that of cotton linters (Cu No. 0·23).

The hydrocellulose was examined for enolic and carboxyl groups by treating the material with diazomethane in ethereal solution. The product contained no methoxyl, an indication that acidic hydroxyl groups are not present in hydrocellulose. The absence of

uronic acid groups was confirmed by the negative results of the application of two standard methods for the estimation of this group.

Glucose was the sole product of the hydrolysis of the hydrocellulose with concentrated sulphuric acid in the cold. The yield of glucose (as crystalline sugar and crystalline methylglucoside) was 91% from the fibre and 92% from the powder.

The hydrocellulose (mixture of powder and fibre) was submitted to direct methylation in the cold by treatment with methyl sulphate and 30% sodium hydroxide solution. After five such treatments a methylated hydrocellulose was obtained which was not homogeneous, being separable into fractions of different viscosity by precipitation from chloroform solution by the addition of light petroleum. The main fraction (representing 70% of the whole) had a methoxyl content of 45·5%. It was hydrolysed by means of a glacial acetic acid–hydrochloric acid mixture. The product of hydrolysis was converted into the corresponding glucosides and the latter mixture was fractionally distilled. The proportion of tetramethyl methylglucoside so separated corresponded to an average chain length for the hydrocellulose (main fraction) of 120 glucose units.

The fibrous fraction of the hydrocellulose was now methylated by an identical process. The main fraction of this methylated derivative (representing 60% of the whole) had an apparent chain length of 200 glucose units as estimated by the end-group method. The amount of the powder fraction of the hydrocellulose available was insufficient for the application of the chemical method of assay. The iodine number of this material corresponded, however, to a chain length of about 70 glucose units.

It seems clear from these experiments that hydrocellulose is simply a cellulose which has undergone degradation in the sense that hydrolysis of some glucosidic linkages has taken place under the influence of the mineral acid used in the preparation of the hydrocellulose. The hydrocellulose is thus constituted of fragments of the original cellulose chain molecules, the essential structure of these fragments being the same as in the parent cellulose. The powder is a form in which the hydrolytic cleavage of the cellulose chains has proceeded further than it has in the fibrous hydrocellulose. It is obvious that each form (powder and fibre) is a mixture of chain molecules of different sizes.

With this conception of the structure of hydrocellulose before us it is interesting to examine the effect of aqueous alkali. When cotton linters was boiled with 0·25N- or 2·5N-aqueous sodium hydroxide, only 3% of it was dissolved. With hydrocellulose, the solubility is very different. Aqueous alkali (0·25N) dissolves 40% of the powder and 12% of the fibre. Aqueous alkali (2·5N) dissolves 60% of the powder and 20% of the fibre. It would seem that the solubility in alkali is inversely proportional to the length of the chain of glucose members.

For comparison cellodextrins, of chain length shorter than that of the hydrocellulose used, were prepared by the acetolysis of cellulose. A cellodextrin with a chain length of 12 units (Haworth and Machemer, J., 1932, 2372) was completely dissolved by boiling 0·25N-sodium hydroxide solution and a dextrin of 18 units was soluble to the extent of 96% in 0·25N-sodium hydroxide and completely soluble in 2·5N-alkali.

Experimental.

Properties of Hydrocellulose.—For the hydrocellulose (prepared by soaking cotton sliver in 5% hydrochloric acid at room temperature; drying first at room temperature and then at 60° and afterwards washing successively with cold water, cold 0·1% aqueous sodium carbonate and cold water) we are indebted to Imperial Chemical Industries Ltd. The material, which retained the fibrous structure of the original cotton, was separated by mechanical teasing into (1) a fine white powder (ash, 5·5; moisture, 1·3%) and (2) fibre (ash, 0·20; moisture, 4·5%) containing very little of the powder form, having the copper numbers already recorded.

Examination for Enolic and Uronic Acid Groups.—(a) Hydrocellulose was dried, immersed first in dry methyl alcohol, and then in dry ether containing diazomethane. After keeping in this solution for 2 days at −10°, the hydrocellulose was collected, washed with methyl alcohol, and dried. The product contained no methoxyl, demonstrating the absence of enolic groups. (b) The hydrocellulose was quantitatively examined for uronic acid groups by the estimation of carbon dioxide evolved on boiling with 12% hydrochloric acid and by the estimation of furfuraldehyde produced under the same conditions. Uronic acid groups were absent.

The Action of Aqueous Alkali on Hydrocellulose.—The loss in weight suffered by the two fractions of hydrocellulose (fibre and powder) and by cotton linters on boiling with water, 0·25N-sodium hydroxide, and 2·5N-sodium hydroxide was determined by treating the materials (in 1 g. lots) with 100 c.c. of the solvent for 1—6 hours. The results are tabulated as % loss in weight of the original material :

Water.

Time of boiling (hrs.)	1	2	3	4	5	6
Hydrocellulose powder	2·6	2·9	2·8	1·7	2·0	2·8
Hydrocellulose fibre	0·8	1·3	0·0	0·5	0·0	2·0
Cotton linters	1·1	1·2	0·2	1·2	0·9	1·8

0·25N-*Sodium Hydroxide.*

Time of boiling (hrs.)	1	2	3	4	5	6
Hydrocellulose powder	23·4	34·6	39·4	39·6	38·8	40·4
Hydrocellulose fibre	9·0	10·5	10·4	12·6	11·8	11·8
Cotton linters	1·2	2·4	2·0	2·0	3·0	3·4

1·2N-*Sodium Hydroxide.*

Time of boiling (hrs.)	1	2	3	4	5	6
Hydrocellulose powder	42·5	43·1	44·2	44·4	42·8	44·5
Hydrocellulose fibre	12·1	12·6	14·0	14·8	15·1	16·3

2·5N-*Sodium Hydroxide.*

Time of boiling (hrs.)	1	2	3	4	5	6
Hydrocellulose powder	49·5	57·9	57·6	60·0	57·0	57·3
Hydrocellulose fibre	15·2	16·9	15·3	17·9	16·5	17·3
Cotton linters	1·7	2·2	2·6	3·2	2·7	2·9

The copper number of the hydrocellulose fibre remaining after alkali extraction was determined in each case :

Time of boiling (hrs.)	1	2	3	4	5	6
Water	1·86	1·50	1·56	1·55	1·54	1·38
0·25N-NaOH	0·45	0·44	0·34	0·35	0·31	0·29
1·2N-NaOH	0·32	0·25	0·39	0·18	0·20	0·18
2·5N-NaOH	0·26	0·13	0·14	0·17	0·14	0·13

Acid Hydrolysis of Hydrocellulose.—The method of Monier-Williams (J., 1921, **119**, 803) was applied to the two hydrocellulose fractions (fibre and powder). The material (5 g.) was kept in contact with 72% sulphuric acid (25 c.c.) for 7 days at room temperature; water (2500 c.c.) was then added, and the solution boiled for 15 hours. The residue after neutralisation with barium carbonate and evaporation to dryness was exhaustively extracted with boiling methyl alcohol and the extract, after decoloration with charcoal, was evaporated to dryness under diminished pressure. Crystalline glucose was separated, and the remaining syrup converted by boiling with 2% methyl-alcoholic hydrogen chloride for 7 hours into the crystalline methylglucoside. The yield of glucose was calculated on the combined yields of crystalline glucose and crystalline methylglucoside. From 4·321 g. of hydrocellulose powder (corrected for ash and moisture) 4·80 g. of glucose were obtained (92%) and from 4·71 g. (corrected) of hydrocellulose fibre, 5·23 g. of glucose (91·4%).

Acetylation.—After treatment of the original hydrocellulose with pyridine and acetic anhydride at 60° for 3 weeks, the product contained only 9·6% of acetyl. Acetylation of both the fibre and the powder fraction was however achieved when treatment with acetic anhydride and acetic acid containing sulphur dioxide and chlorine under the usual conditions was applied. The acetylated hydrocellulose fibre contained acetyl 44·5, moisture 3·8, ash 0·15% and showed $[\alpha]_D^{21°}$ −19·8° in chloroform (*c*, 4·5). The acetylated hydrocellulose powder, obtained in 91% yield, contained acetyl 43·0, moisture 4·5, ash 0·4% and showed $[\alpha]_D^{20°}$ −19·6° in chloroform (*c*, 3·2). The apparent chain length by viscosity measurement in *m*-cresol (K_m, 10^{-3}) was 98 glucose units for the fibre and 65 units for the powder. The iodine value of the latter corresponded to 73 units.

Chain Length of Hydrocellulose by the End-group Method.—(a) *The original hydrocellulose (mixture of fibre and powder).* Hydrocellulose (15 g.) was stirred with 30% sodium hydroxide solution (1500 c.c.) for 4 hours, a solution of methyl sulphate (150 c.c.) in dioxan (150 c.c.) then added, and the mixture stirred at room temperature for 12 hours. Following a further addition of the same quantity of methyl sulphate in dioxan and stirring for12 hours, the fibrous product was collected on a copper sieve and washed with cold water. The product was combined

with a second batch and submitted to further methylation under the same conditions. After the second methylation the product was soluble in dioxan. The product after five such methylations in the cold was boiled with dilute sodium hydroxide solution (to remove methyl sulphate), washed with hot water, and dried. In this way, 160 g. of hydrocellulose (dry wt. 134 g.) gave 134 g. of methylated derivative. This derivative was separated into three fractions by precipitation from a chloroform solution by light petroleum. The main fraction (94 g.) contained 45·5% of methoxyl and the viscosity of a solution in *m*-cresol corresponded to an apparent chain length of 147 glucose units.

The main fraction (91 g.) was hydrolysed by treatment with glacial acetic acid (900 c.c.) and 6% hydrochloric acid (900 c.c.) at 90—95° for 10 hours. The cooled solution was neutralised (to Congo-red) with barium carbonate (250 g.) and evaporated to dryness. The residue was extracted ten times with chloroform (10 l. in all), the extract evaporated to dryness, the syrupy residue dissolved in water (600 c.c.), and the solution extracted with chloroform (fifteen times, with 1500 c.c. in all)—extract A. The aqueous solution was concentrated to 150 c.c. and again extracted with chloroform (six times, 300 c.c. in all)—extract B.

The extracts A and B (after distillation of solvent) were converted separately into the glucosides (2% methyl-alcoholic hydrogen chloride) and fractionally distilled at 0·02 mm. pressure.

Extract A.

Fraction.	$n_D^{22°}$.	Wt. (g.).
1	1·4418	0·398
2	1·4500	1·088

A third fraction which distilled was added to B, and the mixture fractionated as follows :

3	1·4522	0·656
4	1·4535	2·5

Fraction 1 consisted of pure tetramethyl methylglucoside, and fraction 4 of pure trimethyl methylglucoside. It was estimated that fractions 2 and 3 contained respectively 0·326 g. and 0·072 g. of tetramethyl methylglucoside, the total yield of which was 0·796 g., *i.e.*, 0·875%. After correction (J., 1938, 1244) this value indicates a chain length for the hydrocellulose of 123 glucose units.

(b) *Hydrocellulose fibre.* The fibrous fraction of the hydrocellulose (160 g.) was methylated in the cold by the procedure described under (a). The crude product (135 g.) was fractionated in chloroform–light petroleum and the main fraction (80 g.; OMe, 44·8%; apparent chain length from viscosity in *m*-cresol, 360 units) was hydrolysed in the manner already detailed. The A and B fractions (methylglucosides) were united and distilled from a Widmer flask at 0·01—0·02 mm. pressure :

Fraction.	$n_D^{22°}$.	Wt. (g.).
1	1·4420	0·2865
2	1·4517	0·561
3	1·4550	3·2

The total yield of tetramethyl methylglucoside was estimated as 0·424 g., *i.e.*, 0·53%, corresponding, after correction, to a chain length of 200 glucose units.

In each case (a) and (b), the glucosides were characterised by conversion into crystalline tetramethyl glucopyranose (m. p. 85°; $[\alpha]_D^{16°}$ +82·2° in water) and crystalline 2 : 3 : 6-trimethyl glucose (m. p. 115°; $[\alpha]_D^{16°}$ +70° in water).

(c) *Hydrocellulose powder.* The amount of this material that could be conveniently separated by teasing was not sufficient to enable the application of the end-group method to be made. An approximate estimation of the chain length was, however, made from a determination of the iodine number (Bergmann and Machemer, *Ber.*, 1930, **63**, 316) of the powder. The iodine number was 1·89, corresponding to a chain length of 66 glucose units.

The Action of Alkali on Some Cellodextrins.—Raw cotton (100 g.) was added, in portions, to a cooled mixture of acetic acid (375 c.c.), acetic anhydride (375 c.c.), and sulphuric acid (10 c.c.). After keeping at room temperature overnight, the mixture was heated at 30° for 4 days. The dark solution, after centrifuging, was poured into water and the precipitate was washed with water, dried, and extracted with boiling methyl alcohol. The residue (cellodextrin acetates) was fractionated by solution in chloroform and precipitation with light petroleum. Determination of the iodine number of the two main fractions showed the average chain length to be 18 and 12 glucose units.

The 12-unit cellodextrin acetate was completely dissolved by boiling for 4 hours with 0·25N-sodium hydroxide. The 18-unit dextrin acetate was soluble to the extent of 96% in 0·25N-sodium hydroxide and completely soluble in 2·5N-sodium hydroxide.

The authors wish to thank Imperial Chemical Industries Ltd. for the supply of hydrocellulose.

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