392. *Polysaccharides. Part XXXV. Hydrocellulose.*

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Hydrocellulose in a powder form is shown to be constituted on the same plan as cellulose and to differ from the latter only in the number of glucose units constituting the chain molecule. End-group assay on the methylated hydrocellulose showed the average molecular size to correspond to a chain of about 70 glucose units.

WHEN cellulose is submitted, in the cold, to the action of aqueous acids or of oxidising agents, a chemical modification of the substance occurs and this modification finds expression in a more or less complete loss of fibrous structure and in an increased susceptibility to the action of aqueous alkali. The generic name hydrocellulose is applied to the range of degraded products which result from the action of aqueous acids on cellulose, the term " oxycellulose " being employed to describe the products of oxidation. The simplest explanation of the loss of fibrous structure which cellulose suffers under the action of acids is that which postulates a partial breakdown of the cellulose chain with the production of molecules constituted on the same plan as cellulose but containing fewer glucose units. It seemed desirable to investigate hydrocellulose from this point of view and the results now communicated substantiate the hypothesis that hydrocellulose is indeed the product of simple hydrolytic degradation of cellulose.

Hydrocelluloses may be prepared representing varying degrees of hydrolysis of the original cellulose, so that the name covers materials ranging from those scarcely distinguish-

able in appearance from native cellulose to those which have lost all fibrous properties and are friable powders. The hydrocellulose employed in this work belonged to the latter class. It possessed slight reducing properties, was insoluble in water but was soluble to the extent of 30% in aqueous sodium hydroxide. No evidence could be obtained of the existence of carboxyl groups in the hydrocellulose.

The method employed by Haworth and Machemer (J., 1932, 2270) for the determination of the molecular dimensions of cellulose has been applied, without modification, in the present case. An acetate of the hydrocellulose was simultaneously deacetylated and methylated in acetone solution by the addition of equivalent proportions of methyl sulphate and aqueous sodium hydroxide at 45—50°. Fractionation of the hydrocellulose acetate (which was prepared by the usual method employing chlorine and sulphur dioxide as catalysts) in acetone–ether–light petroleum revealed but little heterogeneity and this observation was supported by the properties of the methylated hydrocellulose, which was likewise separated into fractions by precipitation from chloroform solutions. The main fraction of the methylated compound (OMe, 45%) was hydrolysed in cold fuming hydrochloric acid, the resultant mixture of sugars converted into the corresponding methyl glucosides, and these separated by fractional distillation in a vacuum. By this procedure 100 g. of the methylated hydrocellulose yielded 1·62 g. (corrected for losses; see Haworth and Machemer, *loc. cit.*) of tetramethyl methylglucoside. This value corresponds to a chain length for the hydrocellulose of 70 glucose units, a value which is lower than that calculated from the iodine number, namely, 95 units, and higher than the value calculated from the specific viscosity of the methyl hydrocellulose in *m*-cresol (Staudinger's formula, using $K_m = 1 \times 10^{-3}$), namely, 54 units. Nevertheless, all three methods give values of the same order, that is, between 50 and 100 glucose units.

The relationship which obviously exists between chain length and solubility in alkali is being studied.

Experimental.

Hydrocellulose.—The hydrocellulose used in this work was prepared by Imperial Chemical Industries Ltd. by the action of hydrochloric acid on cellulose. It was a fine white powder with slight reducing properties (iodine number, 1·3; copper number, 3·3). It gave a bright yellow colour with iodine. It was insoluble in water and extraction with boiling water (24 hours) or cold water (6 weeks) failed to remove any acidic or reducing material. The hydrocellulose was soluble to the extent of 30% in 15% aqueous sodium hydroxide, but the test for uronic acid residues was negative.

Acetylation of Hydrocellulose.—Hydrocellulose (20 g.) was slowly added to a mixture of glacial acetic acid (200 c.c.), containing chlorine, and acetic anhydride (100 c.c.) containing sulphur dioxide. The mixture was stirred in a ½ l. bottle, and the temperature was not allowed to rise above 10°. After 4 hours most of the solid had dissolved and the mixture was then kept for 16 hours at room temperature. The solution, by this time mobile and slightly opalescent, was diluted to twice its volume with glacial acetic acid. The hydrocellulose acetate was precipitated by passing the solution in a fine stream into tepid water with vigorous stirring. The white, finely divided solid was washed thoroughly with water, then with alcohol, and was dried in a vacuum at 40°. The conditions of the reaction were those of Barnett (*J. Soc. Chem. Ind.*, 1921, **40**, 8T).

This product was not completely acetylated and was therefore reacetylated by treatment at 40° for 16 hours with pyridine (200 c.c.) and acetic anhydride (200 c.c.). The acetate was precipitated, washed, and dried as before. It was purified by solution in chloroform containing 5% of alcohol, and precipitation by light petroleum. The product was then a brittle white solid, which was quite stable when kept for long periods (yield, 32 g.). $[\alpha]_{5780}^{17°}$ −20° in chloroform (*c*, 1·0). Iodine number, 0·6. Acetyl content, 43·2%.

In order to determine whether this hydrocellulose acetate was homogeneous, a sample was subjected to fractionation. The acetate (22 g.) was stirred for 2 hours with cold acetone (500 c.c.) and the mixture was then centrifuged. The portion insoluble in cold acetone (fraction I) became almost completely soluble at higher temperatures (45—50°). The acetate soluble in cold acetone was precipitated in two fractions (II and III) by the addition of ether and light petroleum to the acetone solution. The properties of the fractions are summarised in the following table. The viscosity measurements were carried out in *m*-cresol at 20° (*c*, 0·4 g. per

100 c.c.). The values for the molecular weight and the chain length were calculated from the formula used by Staudinger.

Fraction.	Weight, g.	% Acetyl.	$[\alpha]_{5780}^{20°}$.	$\eta_{sp.}^{20°}$.	Apparent mol. wt.	Apparent chain length.
I	7	39·1	−19·0°	0·31	22,300	77
II	3	44·0	−20·0	0·25	18,000	63
III	11	43·5	−21·2	0·27	19,500	68

c, 0·5 in chloroform containing 10% of alcohol.

Methylated Hydrocellulose.—Hydrocellulose acetate (10 g.) was dissolved in warm acetone (200 c.c.) to form an opalescent solution. It was methylated at 45—50° with 30% caustic soda solution (320 c.c.) and methyl sulphate (120 c.c.). Three-tenths of the methylating agents were added at the beginning of the reaction in addition to sufficient alkali to effect deacetylation. The mixture was stirred vigorously for ½ hour and then the remainder of the reagents was added slowly during 1 hour. The solution was finally heated at 80° until all the acetone had been driven off. The methylated product separated as a cream-coloured granular solid, which was collected on muslin and washed repeatedly with hot water. Yield, 6·3 g. The product was methylated seven times. By repetition of the process, 10 g. of acetate being used in each series of methylations, 100 g. of fully methylated hydrocellulose were collected. This material was extracted several times with boiling ether, which removed the yellow colour, and the product was now a white powder. It was fractionally precipitated from chloroform solution by light petroleum. The properties of the fractions obtained from 84 g. of methylated hydrocellulose are summarised below :

Fraction.	Weight, g.	M. p.	$[\alpha]_{5780}^{20°}$ in $CHCl_3$ (*c*, 0·5).	% OMe.	$\eta_{sp.}^{20°}$.*	Apparent mol. wt.	Apparent chain length.
I	4	207—210°	−5°	42·5	0·172	8,800	44
II	5	205—210	−5	43·5	0·239	12,200	59
III	60	209—212	−7	45·0	0·214	10,000	54

* 0·02 g. in 5 c.c. of *m*-cresol at 20°. By Staudinger's formula.

Another fraction of 11 g. was recovered from the mother-liquors. Its properties were similar to those of fractions I, II, and III. Fraction III was not separable into portions having different properties (Found for fraction III : C, 52·75; H, 8·0. Calc. for $C_9H_{16}O_5$: C, 52·9; H, 7·9%).

Hydrolysis of Methylated Hydrocellulose.—Methylated hydrocellulose (65 g.; properties as fraction III above) was powdered as finely as possible and added gradually to concentrated hydrochloric acid (300 c.c.), the mixture stirred and cooled to 0°, and hydrogen chloride passed into it until it was saturated. The methylated hydrocellulose gradually dissolved, giving a yellow, rather viscous syrup, which became mobile and somewhat darker in colour after 3 days at 0°. The temperature was then raised to 15°, air was bubbled through the solution, and after addition of an equal volume of water the acid was neutralised with barium carbonate. The filtered solution was extracted six times with chloroform (200 c.c. for each extraction). The united chloroform extracts gave on evaporation a syrup (43 g.), which was boiled for 10 hours with 2% methyl-alcoholic hydrogen chloride (1 l.). The solution was neutralised with silver carbonate and the methylated methylglucosides (A) were obtained by evaporation of the solution.

The aqueous solution after extraction by chloroform was evaporated to dryness at 50° under diminished pressure. The solid residue was extracted thoroughly with boiling chloroform and the syrup (23 g.) obtained on removal of the extract was transformed into the methylglucoside as described above. This fraction is referred to as B.

Fraction A. The mixed methylated methylglucosides were distilled from a Claisen flask into a small Widmer flask, and refractionated from the latter. The results are summarised below :

Fraction.	Weight, g.	B. p. (bath temp.)/0·5 mm.	$n_D^{19°}$.	% OMe.
A I	0·9	117—120°	1·4460	61·2
A II	0·3	120—125	1·4506	57·1
A III	4·15	125—135	1·4580	52·0
A IV	5·55	130—140	1·4585	52·1

The remainder of the glucoside in this fraction (38 g.) was distilled directly from the Claisen flask, b p. 130—140°/0·5 mm., $n_D^{16°}$ 1·4578. The still residue was negligible.

Fraction B. This portion was treated in a similar way, the following fractions being obtained on distillation through the Widmer column :

Fraction.	Weight, g.	B. p. (bath temp.)/1 mm.	$n_D^{19°}$.
B I	0·3	135—137°	1·4576
B II	4·0	137—140	1·4580

The remainder (15 g.) was distilled directly from the Claisen flask, giving a main fraction, b. p. 135—140°, with $n_D^{19°}$ 1·4574. There was a small residue (4·5 g.) which did not distil. This was boiled with 2% methyl-alcoholic hydrogen chloride and the product was isolated as before. Most of it distilled at 135—140°/0·5 mm. (bath temp.) and had $n_D^{20°}$ 1·4575. The final portion (0·8 g.) had b.p. 140—150°/0·5 mm. (bath temp.), $n_D^{20°}$ 1·4595, and probably contained some dimethyl methylglucoside (Found : OMe, 48·0%). The refractive indices and methoxyl contents of the fractions indicated that there was 0·9 g. of tetramethyl methylglucosides in fraction A I and 0·15 g. in fraction A II, *i.e.*, 1·05 g. in all. The percentage yield of tetramethyl methylglucoside obtained on hydrolysis of methylated hydrocellulose is therefore 1·62. After correction for experimental losses (Haworth and Machemer, *loc. cit.*) this corresponds to a chain length of 67 glucose units.

Isolation of Crystalline Tetramethyl Glucose from Fraction A I.—Fraction A I (0·5 g.) was boiled with 5% hydrochloric acid (30 c.c.) for 3 hours. The solution was neutralised with silver carbonate, and the filtrate was evaporated to dryness under diminished pressure at 50°. The product was extracted with ether and the extract on evaporation gave tetramethyl glucose (0·4 g.) which crystallised completely. After recrystallisation from light petroleum this had m. p. 88°, alone or when mixed with an authentic sample.

Isolation of Trimethyl Glucose.—Trimethyl methylglucoside (38 g.) was boiled with 5% hydrochloric acid (400 c.c.) for 5 hours. The solution was neutralised with barium carbonate and the filtrate was evaporated to dryness under diminished pressure at 50°. The product was extracted with chloroform, and the extract gave on evaporation 2 : 3 : 6-trimethyl glucose (27 g.) which crystallised completely. It was recrystallised from ether, and had m. p. 120° alone or mixed with an authentic sample.

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