343. *Polysaccharides. Part XIII. The Chain-length of Methylated Cellodextrins.*

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UNDER the conditions of acetolysis cellulose is broken down to molecules of smaller chain-length and although the process can be controlled to a considerable extent to obtain substances representing differing stages of scission, the acetylated products are invariably mixtures. The extreme case is that by which a mixture of glucose and cellobiose acetates is obtained. But intermediate between these substances and cellulose lies a whole range of partly degraded cellodextrins, isolated as their acetates. Some degree of order may be introduced into these products by taking advantage of their solubilities. By an elaborate process of solution and fractional re-precipitation from solvents the compounds are assorted into groups of products having roughly a similar chain-length. The ultimate separations involve a laborious treatment outlined in the experimental section. Five main groups of products were recognised from their solubility differences, decomposition points, rotations, and acetyl content, and their approximate chain-length estimated by the determination of their " iodine value " (which is the degree of reduction observed with Willstätter's reagent—hypoiodite) on the principle worked out by Bergmann and Machemer (*Ber.*, 1930, **63**, 316, 2304).

Our main object was to prepare the methylated representatives of these cellodextrin acetates, which we effected by one direct treatment with methyl sulphate and alkali, and we showed that more than one treatment (Fraction IV, Table II) conferred no advantage. These methylated cellodextrin fractions were each subjected to further fractional solution and precipitation to obtain groups of products having similar properties, and to arrange the several fractions in the order of general homogeneity so far as this is possible. The individual fractions were then hydrolysed and the tetramethyl glucose content of the products was determined. The general experimental treatment was the same as that outlined in the paper by Haworth and Machemer on cellulose (this vol., p. 2270). The greater proportion of the products reveals an average chain-length of 20—25 glucose units corresponding to mol. wts. of 3000—4000 for the parent cellodextrins, whilst others contained from 10 to 14 glucose components. If the further fractional separation which was introduced for the methylated cellodextrins be taken into account, it is seen that these values for the cellodextrin acetates are in general agreement with the estimates of other workers (Bergmann and Machemer, *loc. cit.*; Staudinger and co-workers, *Ber.*, 1930, **63**,

2313, 2331, 3132; 1931, **64**, 1688, 1694, etc.; Meyer and Mark, *Ber.*, 1928, **61**, 2432; Meyer, Hopff, and Mark, *Ber.*, 1930, **63**, 1531; K. Freudenberg and Bruch, *Ber.*, 1930, **63**, 535).

For the original study of the cellodextrins under the name of " biosans " we are indebted to Hess and Friese (*Annalen*, 1926, **450**, 40; compare also Bergmann and Knehe, *ibid.*, 1925, **445**, 1). By an independent method we have shown that the cellodextrins are long-extended molecules consisting of mutually linked glucopyranose units. The chains terminate in end glucose components, each of which can be recognised by the singularity of its properties, in the one case by the occurrence at one terminal position of a tetramethyl glucose component (for the methylated dextrins) and in the other case by the estimation of the reducing property of the glucose component at the reverse end (for the dextrin acetates).

EXPERIMENTAL.

The acetolysis of cellulose was carried out as described by Hess and Friese (*loc. cit.*) and the products were submitted to fractional separation with the series of solvents recommended by these authors. Each of the various solid fractions was dissolved in $CHCl_3$ and pptd. with hot EtOH, and the insol. portion collected.

The products were each hydrolysed by KOH and MeOH, the insol. polysaccharide collected, re-acetylated with Ac_2O and NaAc at 130° for 1 hr., cooled, and poured into ice-water, and the acetates submitted to repeated fractional solution and pptn. (cf. Bergmann and Machemer, *loc. cit.*). The fractions finally separated by this long and laborious treatment are given in Table I. The methylation of each fraction was conducted as described by Haworth, Hirst, and Thomas (J., 1931, 821; see also Haworth and Machemer, *loc. cit.*) for the simultaneous de-acetylation and methylation in acetone (yields, 80—90%).

The methylated products were dissolved separately in $CHCl_3$ (10% solution) and about 4 times this vol. of Et_2O was added at 15° during stirring. As soon as a cloudiness appeared, the Et_2O addition was interrupted and the solution left over-night or until pptn. was complete. Collected on a linen filter, the highly swollen ppt. was easily separated; the filtrate, treated with an equal vol. of light petroleum, gave a second fraction. Vac. evaporation of the filtrate provided the third fraction (Table II). The composition of the fractions was controlled by analysis, but since the C and H values are all similar, only the OMe estimations are recorded.

Hydrolysis of each fractionated portion of the methylated cellodextrins was carried out as described by Haworth and Machemer (*loc. cit.*), and the amount of tetramethyl glucose determined, first as the methylglucoside by repeated fractional distillation in a Widmer flask with column, and finally by hydrolysis to the cryst. tetramethyl glucopyranose. This showed m. p. 90°, $[\alpha]_D$ + 83° (equil. val. in H_2O) (Found: C, 50·65; H, 8·65. Calc.: C, 50·8; H, 8·5%). Since this conversion was almost quantitative, we have recorded in Table II the percentage yield only of the tetramethyl methylglucoside and have calculated therefrom the average number of glucopyranose residues in the methylated cellodextrin fractions which were estimated.

TABLE I.

Fractions of Cellodextrin Acetates.

Fraction No.	Yield, %.	$[\alpha]_D$ in $CHCl_3$.	Sinter and decomp. pt.	AcOH content, %.	No. of glucose residues found by I_2 value.
I	14	−18·1°	274—280°	62·6	21
II	17	−17·9	265—272	63·2	19
III, IV	37 (fractions were combined)	−16·6	252—258	63·0	14
		−16·6	252—258	63·0	14
V	9	−15·6	227—235	64·3	12
VI	13	−14·9	210—215	64·5	12
X	<10	−19·5	290—295	62·5	(Residue of cellulose acetate)

As in the parallel investigation on methylated cellulose, we found that the experimental accuracy of the estimations was subject to a deficiency of 5% in the fractional distillations, and the same correction has been made also for slight losses at the hydrolysis and glucoside formation stages, *i.e.*, a total correction of 10% has been made in the figures as given in Table II.

TABLE II.

Fractionation of Methylated Cellodextrins.

Crude products (before fractionation).		Fractionated products.						
Fract. No. in Table I	Wt., g.	Fract. No.	Wt., g.	$[\alpha]_D$.	OMe, %.	Sinter and decomp. pt.	% Tetramethyl methylglucoside found.	Average number of glucose residues estimated from yield of tetramethyl glucose.
I	23	Ia	22·2	−12·6°	45	230—235°	5·7	21
II	33	IIa	27·5	−12·1	44	229—232	4·6	26
		IIb	3·7	− 9·4	44	218—222		
III	30	IIIa	23·5	−12·5	44	220—235	5·0	24
		IIIb	4·0	−10·0	45	201—203		
		IIIc	1·4	− 5·5	42	155—160		
IV	33	IVa	27·0	−11·7	44	222—225	5·1	24
	(same as Fr. III, but methylated 8 times to study effect)	IVb	4·0	− 9·3	45	205—210	9·0	13 (Fr. IVb, IIb, VII combined)
		IVc	2·0	− 4·5	43	160—165		
V	11 (Fr. Ib, IIc, VIb were united with this)	Va	9·1	− 9·6	44	186—190	8·5	14 (Fr. Va, VIa, IIIb combined)
		Vb	8·4	− 4·4	45	160—163	10·4	11 (Fr. IVc, Vb, IIIc combined)
VI	12	VI	4·5	− 9·0	44	198—203		
VII	2·4	VII	2·4	− 9·8	44	210—215		
VIII	1·0	VIII	1·0	—	40	125—127		

Fr. VII is the united $CHCl_3$ extract of the alkaline aq. methylation solution; Fr. VIII is its most sol. portion.

After the separation of 2 : 3 : 4 : 6-tetramethyl methylglucoside the remaining product was 2 : 3 : 6-trimethyl methylglucoside. From the whole of these distillates 100 g. were refractionated in order to estimate the dimethyl methylglucoside content, which was 4 g. The overall yield of distillates was 90%. No evidence was obtained, from the nature and quantity of the distillates, of the presence of decomposition products and it seemed that little or no decomposition had taken place during the methylation processes.

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