1. Ekwall, P. and Fontell, K. *Acta Chem. Scand.* **10** (1956) 327.
2. Ekwall, P. and Fontell, K. *IX Nord. Kemistmötet, Aarhus, 1956.*
3. Norman, A. *Arkiv Kemi* **8** (1955) 331.
4. *Cf.* Refs. 1—8 in Ref.[1]
5. Ekwall, P. and coworkers. *Unpublished experiments.*

Received December 19, 1956.

Fractionation of Methyl Cellulose Hydrolysate

INGEMAR CROON and BENGT LINDBERG

Institutionen för Träkemi, Kungl. Tekniska Högskolan, Stockholm, Sweden

The distribution of substituents in cellulose derivatives has previously been studied by indirect analytical methods (*cf.* Ref.[1]), the results of which may be rather uncertain and open to some doubt. Spurlin [1] suggested that cellulose ethers should be studied by a different method, involving hydrolysis to glucose and glucose ethers and the fractionation of these by some chromatographic technique. The actual isolation and identification of these products would offer a more reliable basis for calculations. Several authors [2-5] have reported partial fractionations of the products obtained by hydrolysis of methyl cellulose, *e. g.* the fractionation of the three monomethylated glucoses or the fractionation of glucose, mono-, di- and trimethyl ethers. In the present paper the complete fractionation of the eight products in such a hydrolysate is reported. The fractionation was performed on a carbon column using the gradient elution technique. Lindberg and Wickberg[6] separated some methylated sugars by this method and we have recently reported a similar fractionation of the hydrolysate from a hydroxyethyl cellulose[7]. Two components, 6- and 3-*O*-methyl-D-glucose, did not separate by this method but were easily separated by paper chromatography. All components were obtained in a state of purity and identified by their behaviour in paper chromatography and paper electrophoresis, by comparison with authentic samples and by determination of m.p. and optical rotation. Some of them crystallised (see Table 1) and the values for their melting points and specific rotations were in good agreement with those previously recorded.

Experimental. The methyl cellulose investigated was prepared from cotton linters and had a D.S. of 0.90 (OCH_3 15.85, 15.91, 15.97). A sample (1.5 g) was treated with cold 72 % sulphuric acid (16.7 ml). After 30 min at 0° the sample had dissolved completely. It was then diluted with water to 150 ml and heated under nitrogen, first overnight at 60° and finally for 3 h at 100°. The sulphuric acid was neutralised with barium carbonate, the salts removed by filtration and the solution concentrated to dryness (1.460 g). No cellobiose could be detected in the hydrolysate. An aqueous solution of the hydrolysate (50 ml) was added to the top of a carbon column (43 × 3.5 cm) which was then eluted with the following solvents.

Water			1 000 ml
Aqueous	ethanol	0 — 8 %	5 000 »
»	»	8 — 25 »	2 500 »
»	»	25 — 50 »	3 000 »

Fractions (26 ml) were collected and investigated by paper chromatography, paper electrophoresis and determination of the optical rotation (2 dm tube). The result of the fractionation is given in Fig. 1. The 6- and 3-*O*-methyl ethers did not separate well, the former is eluted very slightly faster, and they both contribute to the third peak in Fig. 1, which has a somewhat irregular shape. A small part of the 2-*O*-methyl-D-glucose (second peak) was mixed with the 6-*O*-methyl-D-glucose. Fractions containing s_0 (glucose), s_2(2-*O*-methyl-D-glucose), s_2+s_6, s_6+s_3, s_{26}, s_{36}, s_{23} and s_{236} respectively, were combined, taken to dryness and weighed. In the mixed fraction s_2+s_6, the rather small amount of s_2 was estimated from the shape of the curves. In the mixed fraction s_6+s_3, the proportion between the components was determined by paper chromatography, using methyl ethyl ketone-water (15:1) as solvent. An analytical determination, following the procedure of Hirst, Hough and Jones [8] and a preparative separation on thick filter paper, gave figures in reasonably good agreement, 2.32, 2.43 and 2.26:1, respectively. The yields of each component together with characterising data are given in Table 1.

In a preliminary experiment a larger amount (3.0 g) of methyl cellulose was hydrolysed in the same way and the components fractionated on the same column. A steeper gradient was

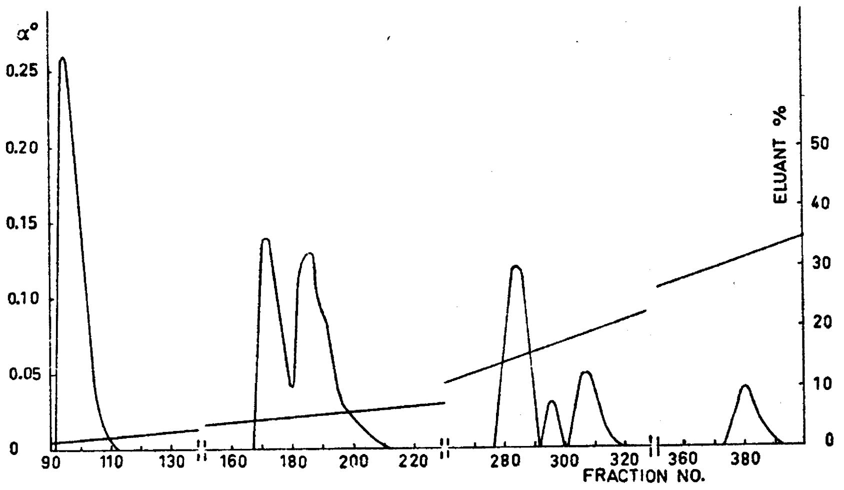

Fig. 1. Chromatographic fractionation of methyl cellulose hydrolysate.

Table 1. Yields and properties of the components from a methyl cellulose (1.5 g) hydrolysate. The components are listed in the order by which they were eluted from the carbon column.

Substance a)	Yield mg	Mol %	$R_G^{b)}$	$M_G^{c)}$	M. p.	$[\alpha]_D^{20d)}$
s_0	540	40.1	1	1	145—146°	+54°
s_2	264	18.2	3.05	0.22	159—160°	+66°
s_6	191	13.2	2.85	0.84	145—147°	+59°
s_3	58	4.0	3.30	0.78	170—171°	+56°
s_{26}	180	11.5	10	0.04		
s_{36}	37	2.4	11	0.52		
s_{23}	85	5.5	14	0.14	115—118°	+52°
s_{236}	85	5.1	—	0.00	117—119°	+68°

a) s_{26} = 2,6-Di-*O*-methyl-D-glucose, a.s.o.
b) Solvent: Ethyl methyl ketone, saturated with water. $R_G = 1$ for glucose.
c) 0.2 M Borate buffer, pH 10. $M_G = 1$ for glucose.
d) In water, $c \simeq 2.0$.

used and practically no separation was obtained between the monomethyl ethers. The separation between the other components, however, was good and the agreement between the two experiments excellent. From both experiments the D.S. of the methyl cellulose could be calculated to 0.90, which is identical with the value calculated from the methoxyl analysis.

The results will be discussed in a forthcoming publication, where the investigation of different methyl celluloses with the present method will be reported.

1. Spurlin, H. M. in Ott, E. and Spurlin, H. M. *Cellulose and Cellulose Derivatives* II, New York 1954.
2. Rebenfeld, L. and Pacsu, E. *Textile Research J.* **24** (1954) 941.
3. Hess, K., Heumann, K. E. and Leipold, R. *Ann.* **594** (1955) 119.
4. Gibbons, G. C. *J. Textile Inst.* **47 : 10** (1956) T 511.
5. Lenz, R. W. and Holmberg, C. V. *Anal. Chem.* **28** (1956) 7.
6. Lindberg, B. and Wickberg, B. *Acta Chem. Scand.* **8** (1954) 569.
7. Croon, I. and Lindberg, B. *Svensk Papperstidn.* **59** (1956) 794.
8. Hirst, E. L., Hough, L. and Jones, J. K. N. *J. Chem. Soc.* **1949** 57.

Received December 21, 1956.