CXV.—*Polysaccharides. Part VI. Trimethyl Cellulose.*

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A METHOD has been devised for the preparation of trimethyl cellulose of maximum methoxyl content by one operation from acetone-soluble cellulose acetate. The details of this process are described and the properties of the trimethyl cellulose fully recorded. In addition a procedure is given for the direct methylation of finely divided native cellulose which requires only three operations for the introduction of the full complement of methoxyl groups. This product is identical with that given by the first method except that it can be obtained in a fibrous form.

Attention is directed to the fact that the molecular weight 2500 determined in camphor by the cryoscopic method is obviously a spurious one, and it would appear that this method of determining molecular weights of cellulose derivatives leads almost invariably to the same minimum value. There can be no doubt that both triacetyl and trimethyl cellulose are much more complex than represented by such a figure. But these results might be interpreted as evidence that little, if any, degradation of cellulose acetate has occurred during its transformation into trimethyl cellulose under the mildest conditions prescribed herein.

EXPERIMENTAL.

Preparation of Trimethyl Cellulose by Simultaneous De-acetylation and Methylation of Cellulose Acetate.—Acetone-soluble cellulose acetate ($CH_3{\cdot}CO$, 40%) (10 g.) prepared from cotton linters was dissolved in acetone (200 c.c.), in a flask fitted with an efficient mechanical stirrer, and kept at 55° during the gradual simultaneous addition of methyl sulphate (120 c.c.) and 30% aqueous sodium hydroxide (320 c.c.). The reagents, the latter of which was filtered through asbestos, were added at the rate of one-tenth of the total every 10 minutes. After 20 minutes, a gelatinous precipitate separated and adhered to the sides of the flask. This was removed by scraping and washed into the solution with a little acetone. An emulsion then formed which persisted until the end of the methylation. The acetone, the volume of which had been maintained at about 200 c.c., was removed by distillation, leaving a mixture of solid and liquid which was filtered hot. The solid was triturated several times with boiling water (1 litre) until the whole of the soluble inorganic impurities had been removed. Trimethyl cellulose was left on the filter as a fine white powder, which was obtained ash-free after trituration with acetone and ether. The yield varied from 85—98% of the theoretical (Found : C, 52·8; H, 7·8; OMe, 45·6. Calc. for $C_9H_{16}O_5$: C, 52·9; H, 7·8; OMe, 45·6%).

Close adherence to the above conditions was necessary in order to obtain in one operation a good yield of the fully methylated derivative. No advantage could be gained by the substitution of 45% aqueous potassium hydroxide for 30% aqueous sodium hydroxide. Lithium hydroxide gave inferior results (yield, 40%; OMe content, 29%). The use of methyl ethyl ketone in place of acetone was also disadvantageous. All the above experiments were carried out at 50—54°. Another series of methylations was performed at lower temperatures (16—20°). In no case could complete methylation be effected in the cold in one operation, but a methylated cellulose containing 43—44% OMe was readily obtainable in theoretical yield by the treatment of cellulose acetate (20 g.), dissolved in acetone (300 c.c.), with methyl sulphate (160 c.c.) and 30% aqueous sodium hydroxide (400 c.c.), the reagents being added simultaneously at 18° during 5 hours. Methylation was complete after one further treatment.

Methylation of Finely Divided Cellulose.—(a) *Cellulose pulp.* The cellulose (pure filter-paper) was cut into small pieces and vigorously stirred with cold water until a thin pulp was formed. The water was removed by evaporation at 100°, and the hard residue rubbed on a metal grater. The finely divided product (4·5 g.), which still retained the original fibrous structure, was stirred into acetone (350 c.c.) and treated in the usual way with methyl sulphate (200 c.c.) and 30% aqueous sodium hydroxide (460 c.c.). The addition of the reagents occupied 4 hours and the temperature was kept at 50—55°. The remaining acetone was removed by evaporation, and the temperature raised to 85°. The crude methylated cellulose was separated by filtration and washed several times with boiling water. The product (yield, 75%) was almost ash-free (0·2%) and was fibrous in structure (Found : OMe, 37·3%). Re-methylation under similar conditions gave a trimethyl cellulose which still retained the fibrous structure (Found : OMe, 45%).

(b) *Finely ground cellulose.* Dry cellulose pulp (5 g., prepared as above), mixed with purified Calais sand (20 g.), was ground in a mortar. The tedious nature of this process was aggravated by the fact that the cellulose at first tended to form flakes which had to be disintegrated before further grinding was possible. After about 2 hours, water (400 c.c.) was added and the grinding continued until the mass was homogeneous. The water was then evaporated and the hard asbestos-like residue was rubbed on a metal grater and ground to a fine powder in a mortar. These operations were repeated until the length of the cellulose fibres was less than 0·2 mm. The mixture of sand (20 g.) and cellulose (5 g.) was treated at 50—55° with methyl sulphate (200 c.c.) and the corresponding amount of 30% aqueous sodium hydroxide. When the reaction was over, the mixture was filtered hot (80°) and the solid was washed several times with hot water, dried in the steam-oven, triturated with acetone, ground to a fine powder, and extracted with boiling chloroform. The methylated cellulose obtained from the chloroform extract by precipitation with light petroleum was ash-free and had OMe, 43·4%. The yield varied from 80—95%. A similar product was obtained in a yield of 50% when the methylation was carried out at 15—16°. On re-methylation trimethyl cellulose was obtained.

Properties of Trimethyl Cellulose.—The figures now given refer to analytically pure material prepared by each of the methods described above and characterised by conversion on hydrolysis into crystalline 2 : 3 : 6-trimethyl glucopyranose (yield, 87%) inasmuch as the physical properties of methylated cellulose alter considerably as the methoxyl content rises from 42% to 45%. M. p. 215—216°, without decomposition. [Material with slightly lower methoxyl content (41—42%) had a much higher m. p. 242—243°.] $[\alpha]_D^{16°}$ − 10·0° in chloroform (*c*, 1·04); $[a]_D^{17°}$ − 24° in benzene (*c*, 0·9); $[\alpha]_D^{0°}$ and $[\alpha]_D^{15°}$ − 25° in water (*c*, 0·5). The rotations in all solvents were numerically smaller for methylated cellulose of lower methoxyl content. Trimethyl cellulose was insoluble in the following solvents at the boiling point: water, acetone, ethyl alcohol, methyl alcohol, ether, light petroleum. It was soluble in hot or cold benzene, toluene, acetic acid, ethyl acetate, pyridine, chloroform, tetrachloroethane, carbon tetrachloride and in hot *iso*amyl alcohol, *iso*amyl acetate or *cyclo*hexanone. Solutions in the last three solvents deposited amorphous trimethyl cellulose on cooling. On slow evaporation of a 10% solution of trimethyl cellulose in a mixture of chloroform and alcohol a portion separated in microcrystalline aggregates. It could not be isolated in sufficient quantity to permit its examination, but the investigation is being continued with the object of comparing this material with the cellodextrin described in the following paper. Trimethyl cellulose was only slightly soluble in water at room temperature and not at all in warm water. The rate of solution in water depended on the physical condition of the substance. Trimethyl cellulose prepared by the above methods dissolved very slowly in ice-cold water, but the rate of solution was much greater for material prepared by dissolution in chloroform and precipitation with light petroleum. The specific rotation, m. p., etc., were not altered by this treatment.

The various samples of trimethyl cellulose differ only in the relative viscosities of their solutions. Material prepared in the cold from cellulose acetates of high viscosity gave more viscous solutions than did material from acetates of lower viscosity. Similarly, the viscosity of solutions of trimethylcellulose varied with the temperature at which the methylation was conducted, low temperatures favouring high viscosity. All solutions, including aqueous solutions, yielded tough films of trimethyl cellulose on evaporation under suitable conditions.

The apparent molecular weight of trimethyl cellulose, determined cryoscopically in camphor, was about 2500. Remarkably consistent results were obtained with different samples of methylated cellulose, including fibrous material. That the value obtained was too low was indicated by the fact that the cellulose acetate from which the trimethyl cellulose had been prepared had the same apparent molecular weight (2500, determined cryoscopically in camphor).

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