# CXVI.—*Polysaccharides. Part VII. Isolation of Octamethyl Cellobiose, Hendecamethyl Cellotriose, and a Methylated Cellodextrin (Cellotetrose ?) as Crystalline Products of the Acetolysis of Cellulose Derivatives.*

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Although the evidence of the isolation of cellobiose by the acetolysis of cellulose has appeared to us to be simply explained by the hypothesis that cellulose is composed of conjugated cellobiose units joined as a continuous chain, it must be admitted that the facts are open to other and less simple interpretations. It has been suggested that cellobiose is a reversion product of the acetolysis and is not preformed in the polysaccharide.

The proof of the constitution of cellobiose (Haworth, Long, and Plant, J., 1927, 2809; compare Haworth and Hirst, J., 1921, **119**, 193) provided evidence for the symmetrical arrangement of β-glucose

residues mutually joined through glucosidic links in the 1 : 4 positions in a continuous chain of pyranose units, and it is clear that only these positions of attachment of β-glucopyranose units satisfy the crystal structure diagram for cellulose. Sponsler and Dore (Colloid Symposium Monograph, New York, 1926, p. 174) have adopted in their interpretation the evidence of the attachment of the glucopyranose units at these positions without necessarily accepting cellobiose as the constituent unit for cellulose. Again, K. Hess (*Ber.*, 1928, **61**, 1982) has regarded cellobiose as a reversion product and has preferred to consider cellulose as a biosan $(C_6H_{10}O_5)_2$, which he claimed to have isolated, associated by the agency of residual valencies.

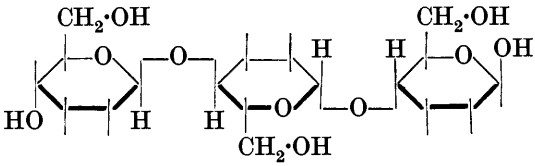
It has been suggested that under the somewhat drastic conditions employed for the acetolysis of cellulose secondary changes may have occurred leading to cellobiose through the intermediary of another less easily recognisable disaccharide.

We have sought evidence for this view by instituting experiments which provided us with specimens of trimethyl cellulose of indubitable quality, having the complete complement of methyl groups (OMe, 45·6%) protecting all exposed hydroxyl positions in native cellulose. Once introduced, these groups exclude the participation of the 2 : 3 : 6-positions from subsequent attack by such reagents as we have employed hereafter.

We have now submitted these specimens of trimethyl cellulose to acetolysis at a temperature not higher than 15° (instead of upwards of 100° as used in the ordinary process for obtaining octa-acetyl cellobiose). The acetylated breakdown products of the trimethyl cellulose were examined after submitting them to simultaneous deacetylation and methylation. A portion of this product (15%) consisted of tetramethyl methylglucopyranoside, and a second portion (18%), distilling at 165°/0·01 mm., crystallised completely and was recognised to be heptamethyl β-methylcellobioside. A third portion (15%) was recognised as hendecamethyl cellotriose, which distilled at about 215°/0·02 mm. and afforded crystalline decamethyl β-methylcellotrioside. A fourth crystalline substance was isolated which we describe as a methylated cellodextrin. This substance gave a molecular weight in camphor of 855, which is in agreement with the value (848) required for a tridecamethyl cellotetrose, but our experience of such results leads us to reserve judgment on this question of its molecular complexity.

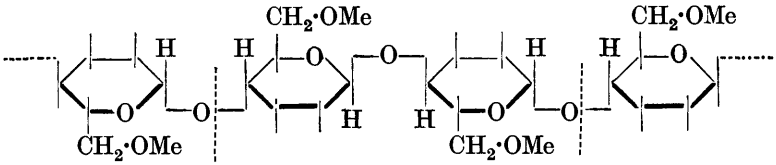
That the crystalline cellotrioside was structurally similar to cellobiose was evident from the ease with which it suffered hydrolysis during 6 hours with 5% aqueous hydrochloric acid to give the products, in the ratio of approximately 1 : 2, crystalline tetramethyl

glucopyranose and crystalline 2 : 3 : 6-trimethyl glucopyranose. Its rate of hydrolysis and general behaviour corresponded with that of a methylated triose constituted on the basis of three glucopyranose residues united by glucosidic links. There was no evidence of any other type of union than that of three such pyranose groups joined in chain formation at positions 1 and 4 in the parent cellotriose and it is clear, from the isolation of tetramethyl glucopyranose as repre-



senting one-third of the product of hydrolysis of the methylated cellotriose, that the left-hand unit is definitely of the six-atom ring form.

The hydrolytic cleavage of the crystalline methylated cellodextrin furnishes the remaining evidence necessary for the proof of the presence of a second such glucopyranose unit. Representing the essential part of the structure of this substance in skeleton as the following, we are able to show that it partly breaks down, by aceto-



lysis at 15°, to yield products which, on simultaneous deacetylation and methylation, are recognised as tetramethyl methylglucopyranoside and crystalline heptamethyl β-methylcellobioside as suggested by the vertical broken lines in the formula. We have therefore accounted for the presence of three consecutive β-glucopyranose units in cellulose.

We have studied in detail the graded acetolysis of trimethyl cellulose under conditions ranging from exceedingly mild to more drastic treatment with reagents. The milder conditions favour the formation of the more complex degradation products, among which the derivatives of the above cellodextrin and cellotriose are recognisable, whilst under the rather more drastic conditions cellobiose and glucose derivatives are mainly represented in the products. It seems clear, therefore, that the breakdown of the cellulose chain is progressive.

## EXPERIMENTAL.

*Acetolysis of Trimethyl Cellulose.*—A solution at 0° of concentrated sulphuric acid (8·2 c.c.) in acetic anhydride (200 c.c.) was added cautiously, with efficient stirring and cooling (ice-bath), to a solution of trimethyl cellulose (20 g.) in glacial acetic acid (250 c.c.). The mixture was shaken at room temperature for 2 hours until it exhibited a green fluorescence. It was poured into water (2·5 litres) and the pale green solution was almost neutralised with solid sodium carbonate. Neutralisation was completed by aqueous sodium bicarbonate. The dark gum which had separated was dissolved in chloroform. The aqueous portion, after extraction with chloroform, was evaporated to dryness and the solid residue was extracted with boiling chloroform. The combined chloroform extracts of two acetolysis experiments were united at this stage and gave on evaporation a viscid gum (54 g.), which was dissolved in acetone (300 c.c.) and subjected to simultaneous deacetylation and methylation by methyl sulphate (160 c.c.) and aqueous sodium hydroxide (150 g. in 350 c.c. of water). The temperature was kept at 35° during the addition of one half of the reagents, and at 50—55° during the addition of the remainder of the reagents, and finally the mixture was heated at 80° for 2 hours. The product was extracted with chloroform in the usual manner and was given two further methylations under similar conditions. It was now a viscid gum (30 g.) which crystallised partly when kept. On distillation under diminished pressure two fractions were obtained, the first (6·0 g.) being mainly tetramethyl methylglucoside, b. p. 75—85°/0·01 mm., $n_D^{14°}$ 1·4462, and the second (7·0 g.), b. p. about 165°/0·01 mm., crystallised completely in rosettes of needles and was recognised as heptamethyl β-methylcellobioside. Recrystallisation from light petroleum (b. p. 40—60°) gave characteristic long needles, m. p. 89—90°, $[\alpha]_D^{22°}$ − 17° in water (*c*, 1·1), in agreement with the constants recorded by Karrer and Widmer (*Helv. Chim. Acta*, 1921, **4**, 174) (Found: C, 53·1; H, 8·5; OMe, 53·7. Calc. for $C_{20}H_{38}O_{11}$: C, 52·8; H, 8·4; OMe, 54·6%).

The material remaining in the distillation flask was a clear reddish-brown glass, which was extracted several times with boiling light petroleum (b. p. 40—60°). The portion (3 g.) insoluble in light petroleum was crystallised several times from ether, giving a methylated cellodextrin (C), m. p. 151—152°, the properties of which are described below.

The portion which dissolved in light petroleum gave two fractions on distillation: (*a*) 5·4 g., b. p. about 208—220°/0·02 mm., and (*b*) 4·7 g., b. p. about 240—250°, $n_D^{16°}$ 1·4740. Fraction (*a*) crystallised

when triturated with light petroleum, but (*b*), which was markedly less viscous than (*a*), could not be crystallised. It remained unaltered in methoxyl content (45%) after methylation with methyl iodide and silver oxide.

Fraction (*a*) was recrystallised twice from light petroleum and then from ether at − 15°, giving *decamethyl β-methylcellotrioside* as silken needles, m. p. 117—118°, $[\alpha]_D^{18°}$ − 14·5° in methyl alcohol (*c*, 2·5), $[\alpha]_D^{20°}$ − 15·1° in water (*c*, 1·95) (compare Freudenberg and Friedrich, *Naturwiss.*, 1930, **18**, 1114). The substance was less soluble in hot than in cold water. The molecular weight, determined cryoscopically in camphor, was 620 (calc., 658) (Found: C, 52·95; H, 8·3; OMe, 51·6. Calc. for $C_{29}H_{54}O_{16}$: C, 52·9; H, 8·3; OMe, 51·8%).

*Hydrolysis of Decamethyl β-Methylcellotrioside.*—Hydrolysis was carried out by heating a solution of the substance (1·3 g.) in 5% aqueous hydrochloric acid (30 c.c.) on the boiling water-bath for 8 hours, the course of the reaction being followed polarimetrically. $[\alpha]_D^{20°}$ − 15° (initial value); + 25° (½ hr.); 39° (1 hr.); 54° (1¾ hrs.); 73° (3 hrs.); 76° (4 hrs.); 77° (6 hrs., constant value). The acid was neutralised with barium carbonate, and the neutral solution, after being diluted with water (30 c.c.), was extracted three times with chloroform. Removal of the chloroform left crystalline tetramethyl glucopyranose, m. p. 76—79°. After recrystallisation from light petroleum (b. p. 60—80°) it had m. p. 86—88°, alone or in admixture with an authentic sample of m. p. 86—89°. $[\alpha]_D^{18°}$ + 84°, equilibrium value in water (*c*, 0·8). The yield of recrystallised material was 96% of the theoretical.

The aqueous portion, after extraction with chloroform, was evaporated to dryness under diminished pressure. The resulting solid was carefully dried and extracted with boiling ether. The ethereal extract gave on evaporation pure 2 : 3 : 6-trimethyl glucopyranose as a colourless crystalline mass (0·91 g.), m. p. 116—119° alone or in admixture with an authentic sample of similar m. p. After recrystallisation from dry ether the substance had m. p. 121—123° and gave $[\alpha]_D^{18°}$ + 108°, 15 minutes after dissolution in water (*c*, 1·14); 82·5° (75 mins.); 69° (5 hours; constant equilibrium value). The yield of recrystallised material was 84% of the theoretical.

*Methylated Cellodextrin* (*Tridecamethyl Cellotetrose ?*).—This substance (C) crystallised from ether in irregular prisms or plates, m. p. 151—152°. It was slightly hygroscopic, soluble in cold water but not in hot water, and was non-reducing. $[\alpha]_D^{18°}$ − 10° in water (*c*, 0·9). The molecular weight, determined cryoscopically in camphor, was 855, which is in agreement with that required for

$C_{37}H_{68}O_{21}$, but this may be a minimum value and no special significance may be attached to it [Found: C, 52·6; H, 8·1; OMe, 45·5. $C_{37}H_{68}O_{21}$ requires C, 52·3; H, 8·1; OMe, 47·5. $(C_9H_{16}O_5)_x$ requires C, 52·9; H, 7·8; OMe, 45·6%. The fully methylated substance, $C_{38}H_{70}O_{21}$, requires OMe, 50·4%].

After further crystallisations from ether or from water and after treatment with silver oxide and methyl iodide the substance had the same m. p. and gave identical analytical figures. Attempts to distil it under diminished pressure were unsuccessful, its b. p. being above 260°/0·01 mm. The substance (3·5 g.), dissolved in glacial acetic acid (50 c.c.), was acetolysed for 7 minutes at 0° with acetic anhydride (35 c.c.) containing concentrated sulphuric acid (0·5 c.c.) and then for 2 hours at 15°; the product was afterwards methylated and it yielded tetramethyl methylglucopyranoside (30% by weight of substance acetolysed) and heptamethyl β-methylcellobioside (25%), m. p. 89°.

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