LXXXIV.—*Note on the Constitution of Cellulose.*

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THE highest product of the acetylation of cellulose (without concomitant hydration) has hitherto been generally regarded as a tetra-acetyl derivative, $C_6H_6O(OCOCH_3)_4$. The constitutional formula of cellulose proposed by Green (*Zeit. Farb. Text. Ind.*, 1904, 3, 97), namely,

contains only three hydroxyl groups, and therefore on acetylation should only give rise to a triacetyl derivative. In all other respects this formula gives a direct and simple explanation of the reactions of cellulose, especially of its conversion by hydrobromic acid into Fenton's ω -bromomethylfurfural and its general behaviour as a "latent" aldehyde.

It therefore appeared to us desirable to reinvestigate the supposed tetra-acetylcellulose with a view to placing its constitution beyond doubt. The product employed for our experiments was kindly supplied to us by Mr. C. F. Cross, to whom our thanks are due. It had been prepared in the usual manner by acetylation of the cellulose regenerated from the xanthate (Cross, Bevan, and Beadle, *Trans.*, 1895, 67, 447). With this product we have determined the acetyl groups by three different methods, namely: (a) by acid saponification according to A. G. Perkin's method (*Trans.*, 1905, 87, 107); (b) by alkaline saponification and direct titration; (c) by alkaline saponification followed by treatment as in method (a).

Method (a) was first employed in the belief that it was less open to possible error than the alkaline saponification. About 0.4 gram of the substance was digested with 30 c.c. of absolute alcohol and 2 c.c. of concentrated sulphuric acid. As soon as the liquid had evaporated

to one-half its volume, fresh alcohol was added, and this was repeated three times. The suspended matter gradually passed into solution, until finally a clear liquid was obtained containing only traces of undissolved cuticle. If the operation is properly conducted, this liquid is almost colourless, but if the latter is allowed to evaporate too far, blackening occurs with evolution of sulphurous acid and vitiation of the analysis. The distillate was received in standard alcoholic potash and titrated with acid in the usual manner.

Acetic acid found :

I.	II.	III.	IV.
61.68	61.36	61.50	63.0 per cent.

Theory for triacetylcellulose, $C_6H_7O_2(OCOCH_3)_3$, = 62.5 per cent.

„ „ tetra-acetylcellulose, $C_6H_6O(OCOCH_3)_4$, = 72.72 per cent.

Another sample furnished us by Dr. F. Marsden gave 59.9 per cent. of acetic acid by this method.

To remove any doubt as to the applicability to carbohydrates of this method of estimating acetyl groups, we have applied it to the penta-acetyldextrose and penta-acetyl-lævulose prepared according to Erwig and Koenigs (*Ber.*, 1889, **22**, 1464, and 1890, **23**, 672).

Penta-acetyldextrose gave 77.68 and 77.25 per cent. acetic acid.

Penta-acetyl-lævulose gave 77.76 per cent. acetic acid.

Theory for each requires 76.92 per cent. acetic acid.

That this method effects a complete saponification of the acetyl-cellulose can scarcely be doubted in view of the fact that at the end of the operation a clear solution is obtained. As, however, it has been suggested that possibly one of the acetyl groups may resist saponification and remain attached to the cellulose residue, we have considered it desirable to repeat the estimation using the method of alkaline saponification. For this purpose, 2 grams of the product were digested for two hours at the boiling point with 100 c.c. of *N*/2-alcoholic caustic soda. After allowing to settle, an aliquot portion of the supernatant liquid was titrated with standard acid.

Acetic acid found :

I.	II.	III.	IV.	V.
59.51	61.24	61.33	59.89	60.92 per cent.

In experiments I, II, and III, ethyl alcohol was used, in experiments IV and V methyl alcohol, the boiling being continued in the last experiment for four hours.

In a third series of determinations, the product obtained by boiling

2 grams of acetylcellulose with 100 c.c. of $N/2$ -alcoholic caustic soda was diluted with alcohol and treated with 10 c.c. of concentrated sulphuric acid, making up the volume with alcohol to 250 c.c. in a stoppered cylinder. Then, after allowing the cellulose and precipitated sodium sulphate to settle, 50 c.c. of the clear solution were drawn off and distilled into standard alcoholic caustic soda, afterwards titrating with acid as usual.

Acetic acid found : 59.8 and 59.75 per cent.

Some slight loss would occur in this procedure, which accounts for the rather lower numbers.

From the above results, it appears to be ascertained beyond doubt that the product of the complete acetylation of cellulose (the so-called tetra-acetylcellulose) is in reality the triacetyl compound. It cannot be doubted that higher acetylated products are obtainable if condensing agents such as zinc chloride or sulphuric acid are present during acetylation, but such products are not true compounds of cellulose, but are derivatives of its hydration products. The highest acetate, therefore, like the highest nitrate and benzoate, corresponds to the presence of three hydroxyl groups in the cellulose molecule.

With reference to the objection which has been raised to Green's formula for cellulose on the ground that so simple a structure is at variance with the physical properties, which seem to indicate a body of high molecular weight, it may be pointed out that the suggested formula is only intended to represent cellulose in its simplest or unpolymerised form, in which, for instance, it may be supposed to exist in an ammoniacal cupric solution. The cellulose of fibres may be regarded either as a physical aggregate of these simple molecules, such as we constantly find occurring in the case of colloidal substances, or as a chemical polymer made up of a number of C_6 complexes of the above structure, united together by means of their oxygen atoms. The former hypothesis appears to us the more probable.

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