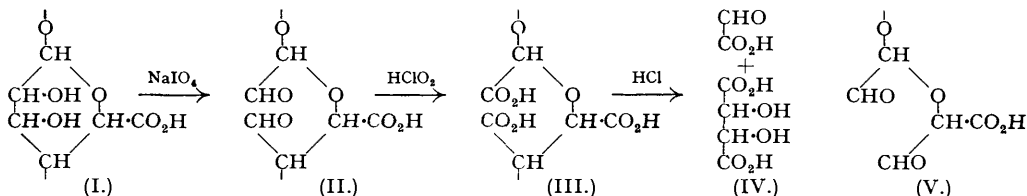


225. Formation of Tartaric Acid by Oxidation and Hydrolysis of Oxycelluloses produced by Dinitrogen Tetroxide.

By FRANK S. H. HEAD.

Kenyon and his co-workers concluded that dinitrogen tetroxide oxidises the primary alcohol groups in cellulose to carboxyl groups. Evidence in support of this has been obtained by oxidising a "dinitrogen tetroxide oxycellulose" with sodium metaperiodate to (II), converting (II) into (III) with chlorous acid, hydrolysing (III), and isolating *mesotartaric acid*.

THE oxidation of cellulose with dinitrogen tetroxide has been studied by Kenyon and his co-workers (*J. Amer. Chem. Soc.*, 1942, **64**, 121, 127; 1947, **69**, 342, 347, 349, 355), who concluded that the primary alcohol groups in the cellulose were preferentially attacked and converted into carboxyl groups of uronic type. A similar conclusion was reached by Maurer and Reiff (*J. Makromolekulare Chem.*, 1943, **1**, 27). "Dinitrogen tetroxide oxycelluloses" accordingly contain units of the structure (I), and it is to be expected that such units would be oxidised by sodium metaperiodate to structural units (II), and further by chlorous acid to units (III); these should be hydrolysed by acid to glyoxylic and tartaric acids (IV). By this series of reactions it has been possible to obtain *mesotartaric acid*, isolated as the acid brucine salt, from a "dinitrogen tetroxide oxycellulose" with an over-all yield of 28%. *meso*Tartaric acid could only be formed among the hydrolysis products if the primary alcohol group in some of the structural units of the original oxycellulose had already been oxidised, though its presence would naturally be expected whether this alcohol group had been oxidised to aldehyde or to carboxyl.



Lucas and Stewart (*J. Amer. Chem. Soc.*, 1940, **62**, 1792), for another purpose, carried out a similar series of transformations with alginic acid, and a much modified version of their method of working was adopted. The oxidation of "dinitrogen tetroxide oxycellulose" with sodium metaperiodate was progressive and there was no sign of a break in the rate of oxidation when

one mole of oxidant had been consumed. This may be connected with the instability to periodate of terminal units, such as (V), containing reactive methylene groups (cf. Huebner, Ames, and Bubl, *J. Amer. Chem. Soc.*, 1946, **68**, 1621), and to the consequent progressive oxidation of the chains from one end.

The oxidation was discontinued at an arbitrarily selected stage. Lucas and Stewart heated the hydrolysate (IV) with baryta to convert the glyoxylic acid into barium glycolate (soluble) and oxalate, and separated oxalic acid from tartaric acid as the copper salt. The latter procedure was found to be superfluous, for brucine oxalate is much more soluble than brucine hydrogen mesotartrate.

Application of the modified procedure to sodium alginate oxidised with sodium metaperiodate gave a 27% yield of brucine hydrogen mesotartrate.

EXPERIMENTAL.

Brucine Hydrogen mesoTartrate.—The authentic salt prepared according to Lucas and Stewart (*loc. cit.*) consisted of colourless needles, $[\alpha]_D^{30} - 22.5^\circ$ (*c.* 0.5 in water), the m. p. of which varied considerably with the initial temperature of the oil-bath; *e.g.*, for a rate of heating of about 6° per min. and an initial temperature of 200° the m. p. (decomp.) was 252° , but with an initial temperature of 250° it was 258° . Lucas and Stewart quote m. p. 259° (uncorr.) and $[\alpha]_D^{30} - 23^\circ$ (*c.* 0.5).

"Dinitrogen Tetroxide Oxycellulose."—The material used was prepared by treating dry, scoured Texas cotton (10 g.) with gaseous dinitrogen tetroxide (16.94 g.) at 20° for 8 days. It contained 11.0% of moisture and 0.78 carboxyl group per C_6 unit as determined by the calcium acetate method (Lüdtke, *Biochem. Z.*, 1934, **268**, 372).

Oxidation of "Dinitrogen Tetroxide Oxycellulose" with Sodium Metaperiodate. Production of (II).—(a) The oxycellulose (0.96 g.) was suspended in a solution of sodium metaperiodate (2.15 g.) in water (100 c.c.) and the whole was kept at 20° . 10-C.c. portions of the liquor were withdrawn at intervals and the excess periodate present was determined by the method of Müller and Friedberger (*Ber.*, 1902, **35**, 2652). The figures for oxygen consumed after various times were :

Time, days	1	2	3
Oxygen consumed, atoms per C_6 unit ...	1.00	1.42	1.62

(b) The oxycellulose (5.00 g.) was suspended in a solution of sodium metaperiodate (10.70 g.) in water (500 c.c.) and the whole was kept at 20° for 48 hours. 20 C.c. were withdrawn for titration as above and the oxygen consumption figure was found to be 1.59. The originally fibrous oxycellulose was completely dissolved or dispersed during the oxidation, the reaction product being a turbid solution from which nothing was precipitated on acidification. The solution was treated with a small excess of potassium iodide (43 g.) and with excess of hydrochloric acid. Iodine was removed by filtration and extraction of the filtrate with methylene chloride. The liquor was neutralised to Congo-red by addition of sodium hydroxide.

Conversion of (II) into (III).—Sodium chlorite (15.5 g.) was dissolved in the above solution, glacial acetic acid (15 c.c.) added, and the whole kept at 20° for 20 hours. Excess of chlorite was destroyed by adding 40% formaldehyde (15 c.c.) and the solution was freed from chlorine dioxide by aeration.

Hydrolysis of (III) and Isolation of mesoTartaric Acid.—The above solution was made acid to Congo-red by addition of hydrochloric acid (20 c.c.) and heated on the steam-bath for 16 hours. It was then made just alkaline by addition of barium hydroxide and heated for a further 3 hours. The precipitate of insoluble barium salts was collected, well washed, and dried at 110° (4.0 g.). It was powdered, suspended in a little water containing the theoretical amount (28.3 c.c.) of N-sulphuric acid (assuming precipitate to be barium tartrate), heated on the steam-bath for a short time, and filtered. The filtrate (90 c.c.) was halved. Half was treated with alcohol (45 c.c.) and made alkaline to litmus by adding an excess of brucine. The second half was then added, and the mixture was heated on the steam-bath for 3 hours, diluted with water (150 c.c.), cooled, and extracted three times with chloroform. The aqueous portion was concentrated to about 35 c.c. on the steam-bath and left over-night. Brucine hydrogen mesotartrate separated as colourless needles, m. p. 252° *. The yield (3.11 g., dried at 110°) corresponded to 28% of the theoretical, assuming that the original oxycellulose was a polymer containing 78% of anhydroglucuronic acid units, the remainder being anhydroglucose units. Recrystallisation gave material of m. p. 257° * which did not depress the m. p. of an authentic specimen; $[\alpha]_D^{30} - 22^\circ$ (*c.* 0.5).

Parallel Experiments with Sodium Alginate.—Commercial sodium alginate (4 g.; corresponding to about 3.4 g. of pure material) was oxidised with sodium metaperiodate (6.6 g.) dissolved in water (*ca.* 250 c.c.). After 4 days at 20° the titre of a weighed portion indicated an oxygen consumption of 1.6 atoms per mannuronic acid unit. The subsequent operations were closely similar to those described above; the yield of brucine hydrogen mesotartrate was 2.5 g. or 27%. Some gum separated during the chlorite oxidation but redissolved during the subsequent hydrolysis.

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* Uncorrected m. p.s determined with an initial bath temperature of 250° .