95. *The Synthesis of Dimethyl Dimethylene* l-*Idosaccharate.*

By W. G. M. Jones and L. F. Wiggins.

Methylenation of the calcium salt of *l*-idosaccharic acid has been effected, and the resulting dimethyl dimethylene *l*-idosaccharate shown to be identical with the ester obtained by the epimerisation of dimethyl dimethylene *d*-glucosaccharate and dimethyl dimethylene *d*-mannosaccharate.

The transformations taking place when dimethylene glucosaccharic acid or its dimethyl ester is treated with boiling baryta solution have been described by Haworth, Jones, Stacey, and Wiggins (this vol., p. 61). The product in either case was an isomeric dimethylene saccharic acid which could likewise be obtained by the treatment of dimethyl dimethylene *d*-mannosaccharate with hot alkali. It was postulated that the reaction taking place was one of epimerisation at C_5 in the case of the *d*-glucosaccharate and at C_2 and C_5 in that of the *d*-mannosaccharate, leading to the formation of the hitherto unknown dimethylene *l*-idosaccharic acid. This deduction has now been completely verified by the synthesis of the dimethyl ester of dimethylene *l*-idosaccharic acid from *l*-iditol.

l-Iditol was prepared by the hydrogenation of *l*-sorbose over Raney nickel, and separated from the accompanying *d*-sorbitol by acetylation of the product and subsequent fractional crystallisation of the hexa-acetates. Catalytic deacetylation of the *l*-iditol hexa-acetate gave crystalline *l*-iditol. Oxidation of the alcohol was effected by means of nitric acid, and *l*-idosaccharic acid isolated as the calcium salt. Methylenation of this salt by treatment with paraformaldehyde and concentrated sulphuric acid, followed by esterification with methyl alcohol, gave dimethyl dimethylene *l*-idosaccharate, shown to be identical with the material obtained by epimerisation of dimethyl dimethylene *d*-gluco- and *d*-manno-saccharate.

EXPERIMENTAL.

l-*Iditol Hexa-acetate.*—*l*-Sorbose (50 g.) in water (300 c.c.) was hydrogenated over Raney nickel at 145° and 90 atm. for 6 hours. The filtered solution was evaporated to a syrup, which was boiled for ½ hour with acetic anhydride (200 c.c.) and fused sodium acetate (25 g.). The product was poured into ice-water and the crystalline precipitate which separated was filtered off, washed with water, dried, and fractionally recrystallised from alcohol; two fractions were thus obtained, *viz.*, hexa-acetyl *l*-iditol (30 g.), m. p. 122°, $[\alpha]_D^{15°}$ −24·8° (in chloroform; *c*, 5·63), and hexa-acetyl *d*-sorbitol (35 g.), m. p. 98°. Bertrand (*Bull. Soc. chim.*, 1905, **33**, 166) gives m. p. 121·5° and $[\alpha]_D$ −25·7° (in chloroform) for hexa-acetyl *l*-iditol.

l-*Iditol.*—Finely powdered *l*-iditol hexa-acetate (14 g.) was suspended in dry methyl alcohol (300 c.c.), sodium (50 mg.) added, and the mixture shaken overnight until solution was complete. Evaporation gave *l*-iditol in quantitative yield as a syrup which slowly crystallised on keeping in a desiccator. It was used as such for the following experiment.

Oxidation of l-*Iditol.*—*l*-Iditol (5 g.) was vigorously oxidised by warming with 60 c.c. of nitric acid (*d* 1·15) on the boiling water-bath; excess of nitric acid was removed by repeated evaporation with addition of water from time to time, and the syrup finally obtained was diluted and neutralised at 70° with sodium hydroxide solution. Hydrated calcium chloride (5 g.) was then added, and the precipitated calcium *l*-idosaccharate (6 g.) removed by filtration, washed with water, and dried in air.

Methylenation of Calcium l-*Idosaccharate.*—The calcium salt (3 g.) was mixed intimately with paraformaldehyde (2 g.), concentrated sulphuric acid (1·5 c.c.) added, and the mixture stirred to a thick paste and warmed over a bare flame for 30 minutes. Dry methyl alcohol was added, and insoluble calcium sulphate filtered off. The methyl-alcoholic solution was boiled under reflux for 2 hours, and the product crystallised from the hot solution. The crystals were collected and recrystallised from aqueous methyl alcohol. A further quantity of the crystals was recovered from the mother-liquors of the esterification; total yield 0·9 g. (Found: C, 45·8; H, 5·3. Calc. for $C_{10}H_{14}O_8$: C, 45·6; H, 5·5%). The crystals melted at 296° and were dimethyl dimethylene *l*-idosaccharate, the m. p. showing no depression on admixture with a specimen of this material prepared by epimerisation of dimethylene *d*-glucosaccharic acid.

The authors are indebted to Professor W. N. Haworth for his interest and to Imperial Chemical Industries, Ltd. (Dyestuffs Division), for a grant in aid of this work.

The A. E. Hills Laboratories,
The University, Edgbaston, Birmingham.

[*Received, April* 24*th*, 1944.]