

XXXI.—*The Degradation of l-Arabinose.*

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THE degradation of *l*-arabinose to erythrose, effected first by Wohl (*Ber.*, 1899, **32**, 3667) and Ruff (*Ber.*, 1901, **34**, 1365) and later by Weermann (*Rec. trav. chim.*, 1917, **37**, 16), has now been achieved by Zemplén's method (*Ber.*, 1926, **59**, 1254; 1927, **60**, 165), viz.,

by the action of sodium methoxide on tetra-acetylaronitrile in chloroform solution. The tetrose was identified in the form of its osazone, but the syrup containing it could not be freed from inorganic salts. A purer product, dextrorotatory and almost ashless, was obtained by the action of barium hydroxide and silver carbonate on arabinonitrile.

The yields of erythrose (calculated from the reducing power) produced in these two methods were 40% and 13%, respectively, of the theoretical yields, but in each case the weight of erythrosazone actually isolated was very small owing to the difficulty of extracting it from its syrupy mother-liquor.

The erythrose obtained by the first method gave mesotartaric acid on oxidation with nitric acid (compare Anderson, *Amer. Chem. J.*, 1909, 42, 429).

EXPERIMENTAL.

Arabinoseoxime was prepared by Wohl's method (*loc. cit.*), but the alcoholic solution containing the sugar and hydroxylamine was heated for an hour at 60° after all the arabinose had dissolved. The nitrile was obtained by heating the oxime with acetic anhydride and anhydrous sodium acetate for an hour at 90°, the quantities being those recorded by Wohl (*loc. cit.*); the product was whiter than that obtained by Wohl's procedure and melted at 119—120° after recrystallisation from alcohol (Wohl gives m. p. 117—118°).

Degradation of Tetra-acetylaronitrile.—A solution of 5 g. of the nitrile in 10 c.c. of chloroform was treated, according to the directions given by Zemplén (*loc. cit.*) in the case of glucose, with a solution of 1.2 g. of sodium in 10 c.c. of absolute methyl alcohol; the addition-compound formed was decomposed by the addition of 20 c.c. of water. The aqueous solution was acidified, separated from the chloroform, and evaporated in a vacuum. The residual mixture of syrup and solid was treated with absolute ethyl alcohol and the extract was filtered and evaporated; these operations were repeated twice and the final product was dissolved in and made up to 25 c.c. with water. A test by Bertrand's method indicated the presence of 0.840 g. of reducing matter (calculated as glucose) in the solution. Nitrile (possibly arabinonitrile) also was present, as 10 c.c. of the solution when treated with ammoniacal silver oxide solution gave 0.0244 g. of silver cyanide (corresponding to only 2.8% of the original tetra-acetylaronitrile).

A portion (5 c.c.) of the solution was heated with acetic acid and phenylhydrazine in a boiling water-bath for 3 hours, a dark syrup separating which partly solidified in the course of 2 days. It was then repeatedly extracted with boiling water until this deposited

no osazone on cooling. The osazone, after recrystallisation from water and from benzene, melted at 164—165° (yield, 0.03 g.).

The yellow aqueous solution of erythrose was treated with a little bone-black, filtered, and concentrated in a vacuum, the residue was extracted with absolute alcohol, and the filtered extract was evaporated in a vacuum. The colourless, dextrorotatory syrup obtained, which still contained inorganic material, gave, on treatment with naphtharesorcinol, a dark red precipitate, the dark cherry-red alcoholic solution of which gave an absorption band in the green region and other weaker bands near the D line of the spectrum.

Degradation of Arabonitrile.—Tetra-acetylaronitrile (5 g.) was heated with 5 c.c. of 10% sulphuric acid in a boiling water-bath until a precipitate was no longer formed on dilution. The solution was cooled and shaken with 3 g. of barium hydroxide and 0.750 g. of silver carbonate. After 24 hours, when all the nitrile had disappeared, the solution, after being faintly acidified with sulphuric acid and filtered, was freed from sulphuric acid by the addition of barium hydroxide (calculated amount), treated with bone-black, and filtered. It then had a reducing power (Bertrand) corresponding to 0.250 g. of glucose. On evaporation a colourless, dextrorotatory syrup was obtained, which gave a strong reaction with naphtharesorcinol and yielded an osazone, m. p. 163.5—164.5°.

Oxidation of Erythrose to mesoTartaric Acid.—The syrup (reducing power corresponding to 2.05 g. of glucose) obtained from 15 g. of tetra-acetylaronitrile as described above was diluted with 5 c.c. of water and treated with 5 c.c. of nitric acid (*d* 1.40). After 10 days, the mixture was diluted with more water and boiled to expel nitrous fumes, and lead salts were precipitated by addition of lead acetate. These were converted in the usual way (hydrogen sulphide; calcium chloride and ammonia) into a mixture of calcium oxalate and mesotartrate. The latter was extracted with glacial acetic acid and the solution was diluted with water and evaporated, yielding 0.492 g. of hydrated calcium mesotartrate (Found: loss at 170°, 22.6; CaO, 23.6. Calc. for $C_4H_4O_6Ca, 3H_2O$: H_2O , 22.3; CaO, 23.1%).

One of us (V. D.) is indebted to Professor Zemplén for permission to use his method of degradation and for information concerning it.

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