457. *The Molecular Weight of* l-*Erythrose.*

By VENANCIO DEULOFEU.

GLYCOLLALDEHYDE (Fenton and Jackson, J., 1899, **75**, 577), dihydroxyacetone, and lactaldehyde, which contain an alcoholic hydroxyl group adjacent to carbonyl, show twice the theoretical molecular weight in fresh aqueous solutions. Glyceraldehyde (Wohl and Neuberg, *Ber.*, 1900, **33**, 3095) and similar compounds (Bergmann and Kann, *Annalen*, 1924, **428**, 278) also exhibit association.

From the results obtained by Helferich and his collaborators with γ-hydroxyaldehydes (see especially Helferich and Gehrke, *Ber.*, 1921, **54**, 2640) it was to be expected that tetroses would have normal molecular weights in solution, and this has now been found to be so for erythrose, for which molecular weights of 130 and 132 have been obtained in two experiments (calc., 120). These results were obtained before Freudenberg's paper (*Ber.*, 1932, **65**, 168) on crystalline *d*-threose appeared.

Erythrose, which does not give Angeli's aldehyde reaction and responds only slowly to the Schiff test, may be regarded as trihydroxytetrahydrofuran, the simplest representative of the furanose class of sugars (Haworth, "Ring Structure in the Monosaccharides, etc."; Dixième Conférence de l'Union International de Chimie, p. 42).

Tetra-acetyl arabononitrile has been prepared from arabinose oxime, and erythrose-diacetamide from triacetyl erythrose. The latter result confirms the work of Brigl, Mühlschlegel, and Schinle (*Ber.*, 1931, **64**, 2921) on the necessity for a free aldehyde group for this type of condensation.

Experimental.

Tetra-acetyl Arabononitrile.—To a clear cool solution of arabinose oxime (1 g.) in anhyd. pyridine (2 c.c.), Ac_2O (5 c.c.) was added, the temp. being kept below 70°. After remaining for 24 hr. at room temp., the solution was poured into H_2O (30 c.c.). The pptd. syrup, after solidifying, was washed with H_2O, dried, and crystallised from EtOH until it had m. p. 119—120°, alone or mixed with the nitrile prepared in the usual way.

Erythrose-diacetamide.—Triacetyl erythrose (0·5 g.) was treated with a mixture of 96% EtOH and conc. NH_3 aq. (5 c.c. of each), after 24 hr. the solution was evaporated in vac., and the residue treated with abs. EtOH–Et_2O and seeded with erythrose-diacetamide. The crystals formed after some hr. were recrystallised from H_2O; m. p. and mixed m. p. 210°.

Triacetyl Erythrose-diacetamide.—Erythrose-diacetamide (1 g.) was warmed with 5 c.c. of pyridine and 3·5 c.c. of Ac_2O until it dissolved. The solution was kept for 24 hr. at room temp. and then evaporated in vac. over KOH and H_2SO_4. The residue of *triacetyl erythrose-diacetamide*, after crystallising four times from EtOH–Et_2O, formed colourless crystals, m. p. 147°, very sol. in H_2O, $CHCl_3$, and EtOH and sparingly sol. in Et_2O; $[\alpha]_D^{20°}$ +31·7° in H_2O. The substance reduced Fehling's solution only after prolonged heating (Found: N, 8·25. $C_{14}H_{22}O_8N_2$ requires N, 8·1%).

Erythrose Benzylphenylhydrazone.—A solution of erythrose-diacetamide (5 g.) in H_2O (300 c.c.) was boiled with 25% H_2SO_4 (15 c.c.) for 1 hr., concentrated to 25 c.c. in vac. at a low temp., extracted continuously with Et_2O, diluted, and neutralised with $Ba(OH)_2$. Dil. AcOH was then added drop by drop, and the faintly acid solution filtered and evaporated in vac. to dryness. The residue was extracted with abs. EtOH so long as the extracts reduced Fehling's solution. The combined extracts were titrated for reducing sugars (expressed as glucose), the necessary quantity of benzylphenylhydrazine added, and next day the solution was evaporated in vac., the residue extracted with warm C_6H_6, and the extract treated with ligroin (½ vol.). Any ppt. produced was removed quickly, and the filtrate kept; cryst. erythrose benzylphenylhydrazone then separated, m. p. 102—103°. Some prepns. failed to give a cryst. hydrazone.

Calcium Arabonate.—The general method of Hudson and Isbell (*J. Amer. Chem. Soc.*, 1929, **51**, 2225) was simplified. A solution of arabinose (15 g.) and barium benzoate (60 g.) in H_2O (750 c.c.) was cooled to 3° and treated with Br (6·1 c.c.). The solution was shaken for some min., benzoic acid separating, and then kept in the dark for 40 hr. until the Fehling reaction was negative. The slight excess of Br was removed in a stream of air, the Ba pptd. with 6*N*-H_2SO_4, and the filtered solution shaken with $CHCl_3$, which extracted the dissolved benzoic acid and the last trace of Br. The solution was then boiled with $CaCO_3$ and concentrated in vac. to 90 c.c. After some time, hydrated calcium arabonate ($5H_2O$) crystallised; yield, 21 g. (90%).

l-Erythrose.—The calcium arabonate was recrystallised from H_2O (charcoal),

dried in vac. at 100°, and degraded by Ruff's method (*Ber.*, 1899, **32**, 3672) to erythrose, which was isolated as the benzylphenylhydrazone.

Erythrose benzylphenylhydrazone (10 g., obtained by the two methods above indicated) was treated in a boiling water-bath with 20 c.c. of a freshly prepared solution of formaldehyde. After 20 min. the formaldehyde benzylphenylhydrazone was removed, and the filtrate extracted with Et_2O for some hr. and then evaporated below 30° in vac. The almost colourless syrupy residue was dissolved in abs. EtOH, the solution filtered and evaporated in vac. at room temp., and the syrupy residue kept over P_2O_5 and KOH in a desiccator until its wt. was constant. The product was a colourless ashless syrup, $[\alpha]_D^{20°}$ in H_2O, + 1·3° (initial) and + 22·1° (final value). The substance slowly coloured Schiff's reagent.

Molecular Weight of l-*Erythrose.*—Two determinations were made with the dry erythrose in the usual Beckmann apparatus. (*a*) 0·1962 G. in 17·46 g. H_2O gave Δ 0·16°; *M*, 129·9. After 3 hr. the same depression was obtained. (*b*) 0·2796 G. in 17·83 g. H_2O gave Δ 0·22°; *M*, 132. After 4 hr., Δ was 0·23°, corresponding to *M*, 126·2. (Calc.: *M*, 120).

Instituto de Fisiología, Buenos Aires. [*Received, July 18th*, 1932.]