CCCXXIV.—*Formation of* l-*Threose.*

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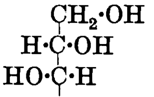
l-THREOSE is the only sugar from glycerose to the pentoses inclusive not hitherto synthesised. We do not know even the sign of its rotatory power, for Maquenne (*Compt. rend.*, 1900, **130**, 1403) and Ruff (*Ber.*, 1901, **34**, 1307), who obtained evidence of the formation of its optical antipode, left this undetermined.

We synthesised the diacetamide compound (annexed formula) of *l*-threose by the degradation of tetra-acetyl *l*-xylononitrile according to Wohl's method, and hydrolysed it by means of dilute sulphuric acid in a boiling water-bath until a constant rotatory power was attained. From examination of this solution (compare Wohl, *Ber.*, 1899, **32**, 3667), we assign a specific rotatory power of $[\alpha]_D^{20^\circ}$ $-24\cdot6^\circ$ to *l*-threose.



$$\begin{array}{c} CH_2\cdot OH \\ | \\ H\cdot C\cdot OH \\ | \\ HO\cdot C\cdot H \\ | \\ CH(NHAc)_2 \end{array}$$

Owing to lack of material, the sugar could not be isolated in a pure state, but its formation was confirmed by the preparation of an osazone, m. p. 165—166° (erythrosazone has m. p. 165°), from the hydrolysed solution.

EXPERIMENTAL.

From *d*-saccharolactone (250 g.), *l*-gulonolactone was obtained by reduction (Fischer and Piloty, *Ber.*, 1891, **24**, 521), and by oxidation of the latter according to the method of Fischer and Ruff (*Ber.*, 1900, **33**, 2142) the necessary *l*-xylose (3·1 g.) was prepared, m. p. 141°.

l-*Xylose Oxime.*—This oxime was prepared by treating the sugar (3·1 g.) with an excess of hydroxylamine in alcoholic solution. After all the xylose had dissolved, the solution was heated for 1 hour at 60° in a water-bath, left for two days at room temperature, and then evaporated in a vacuum. The resulting syrup (3·6 g.) could not be induced to crystallise even when kept for 3 months in a desiccator.

Tetra-acetyl l-*Xylononitrile.*—The syrupy oxime (3·5 g.) was treated with acetic anhydride (16 c.c.) and recently fused sodium acetate (3 g.), the mixture being heated very slowly until reaction was complete; the resulting dark syrup was poured into 25 c.c. of cold water and soon solidified. More of the nitrile separated on being kept for a day, and the whole was collected, well dried, and extracted with ether (Soxhlet), in which the dark by-products were insoluble. The ethereal extract was red, but evaporation of the solvent and recrystallisation of the residue from alcohol yielded the pure *nitrile* (3·05 g.; 48%) as white crystals, m. p. 82° (Found : CN, 8·0. $C_{13}H_{17}O_8N$ requires CN, 8·2%), soluble in ether or alcohol, very soluble in chloroform, and almost insoluble in water.

l-*Threose Diacetamide.*—Tetra-acetyl xylononitrile (3 g.) was dissolved in 10 c.c. of alcohol and treated with the silver oxide obtained from 2 g. of silver nitrate previously dissolved in 15 c.c. of 22% ammonia solution. The mixture became somewhat warm and a precipitate of silver cyanide immediately appeared. After two days' standing, this precipitate was collected, the filtrate evaporated in a vacuum to a syrup, the latter dissolved in 50% alcohol, refiltered if necessary, and the silver removed by hydrogen sulphide. The liquid was again evaporated to a syrup, which was treated with a mixture of absolute alcohol (1 vol.) and absolute ether ($\frac{1}{2}$ vol.). The crystalline precipitate produced on standing was collected and recrystallised from 95% alcohol (charcoal); yield 0·66 g., *i.e.*, 30%. (All the evaporations were carried out below 50°.) The *diacetamide* compound (Found : N, 13·0. $C_8H_{16}O_5N_2$ requires N, 12·7%) is a white solid, m. p. 165—166°, very soluble in water, moderately soluble in warm alcohol, but very sparingly soluble in cold, and insoluble in ether; it has a sweet taste.

Hydrolysis of the Diacetamide.—0·5841 G. of the diacetamide was dissolved in 25 c.c. of *N*/3-sulphuric acid and then had $[\alpha]_D - 7·68°$. The solution was heated in a boiling water-bath, and after ½ hour its rotatory power was $[\alpha]_D - 24{\cdot}8°$ (calculated on the weight of *l*-threose formed), and after another 15 minutes $[\alpha]_D - 24{\cdot}4°$ (mean of these two rotations, $[\alpha]_D\ 24{\cdot}6°$). On further heating, the solution turned yellow.

The sulphuric acid solution was neutralised quantitatively with barium hydroxide, treated with bone-black, and filtered. The filtrate was evaporated under diminished pressure to 5 c.c., thus giving approximately a 5% solution of threose. This solution reduced Fehling's solution in the cold, gave a strong reaction with α-naphthol, and with naphtharesorcinol yielded a dark precipitate giving a reddish-violet solution in alcohol, which showed slight violet fluorescence, and absorption in the green and near the D line region of spectra. No reaction was obtained with resorcinol. (Neuberg, *Z. physiol. Chem.*, 1901, **31**, 564, found that a threose prepared by the oxidation of erythritol by sodium hypobromite solution gave a positive resorcinol reaction.) The remainder of the solution was treated with phenylhydrazine acetate and heated for 3 hours in a boiling water-bath; the precipitated osazone was recrystallised from benzene and then melted at 165—166°.

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