LIX. THE HYPERACETYLTATION OF ALDOSES.

By NORMAN WINGATE PIRIE.

From the Biochemical Laboratory, Cambridge.

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MICHEEL *et al.* [1935] have described the synthesis of heptaacetyl-*dl*-galactose and of heptaacetyl-*d*-galactose; this is the first instance of the diacetylation of the aldehyde group in a sugar. In the preceding paper I have described the isolation of *dl*-galactose from agar as the heptaacetyl derivative. The method of synthesis used by Micheel *et al.* is rather laborious; since sugar derivatives of this type are of interest for a number of reasons, a simpler and apparently general method for their preparation has been worked out. The diethylmercaptal or the acetylated diethylmercaptal of the sugar has been used in each case but it is probable that any other derivative of the aldehydic form of the sugar would do instead provided that it could break down under the conditions of hyperacetylation to give the free aldehyde.

Six hyperacetylated sugars have been made and all but one crystallise very readily. The small optical rotation and the readiness with which the melting points are affected by impurities diminish their usefulness for characterisation but the ease with which they can be crystallised even from a very crude solution suggests that they may prove useful for the separation of sugars.

Heptaacetyl-d-galactose.

Unsuccessful attempts were made to prepare heptaacetyl-*d*-galactose from *d*-galactose, *d*-galactosemethylphenylhydrazone, β -pentaacetyl-*d*-galactopyranose and β -pentaacetyl-*d*-galactofuranose [Schlubach and Prockownick, 1930] by acetylation under the conditions used with agar. In the first case α -pentaacetyl-*d*-galactopyranose (m.p. 96° , $[\alpha]_D + 103^\circ$ and acetyl content 55%) was isolated and in the last some pentaacetylgalactofuranose was recovered unchanged. In the other two cases no crystalline material could be isolated.

Pentaacetylaldehydo-*d*-galactose and its diethylmercaptal were therefore prepared [Wolf from, 1930] and these substances, together with galactose diethylmercaptal were found to give heptaacetyl-*d*-galactose on acetylation. There is considerable destruction and the yield is always low but it can be improved by using a shorter time of incubation and less sulphuric acid than is possible in the case of agar. If 2 g. of pentaacetyl-*d*-galactose diethylmercaptal are suspended in an ice-cold mixture of 20 ml. acetic anhydride and 1 ml. conc. H_2SO_4 , 0.7 g. of the heptaacetate can be isolated after 24 hours at 37° by the method used for the isolation of heptaacetyl-*dl*-galactose.

Large well-formed crystals separate when heptaacetyl-*d*-galactose is crystallised from alcohol but these contain alcohol and have a low m.p. ($85-90^\circ$). This alcohol is not readily removed in a desiccator. Small crystals are obtained from water or methyl alcohol and needles up to 1 cm. long are formed by the aggregation of an emulsion when heptaacetylgalactose is dissolved in 20 parts of boiling 25% methyl alcohol and then allowed to crystallise at 37° . After drying at room temperature *in vacuo* it melts at 106° and has $[\alpha]_D + 4.0^\circ$ in chloroform solution. (Found: C, 48.76; H, 5.80; acetyl 62.2%. Calculated: C, 48.76; H, 5.73; acetyl, 61.2%.)

When compared with galactose this substance is found to contain 36 % of reducing sugar by the Hagedorn-Jensen method and after acid hydrolysis galactose can be isolated in the usual way. This galactose, at equilibrium, had $[\alpha]_D^{19} + 80.3^\circ$ in water.

Heptaacetyl-d-mannose.

The pentaacetate of *d*-mannose diethylmercaptopal has not apparently been made before. Mannose mercaptopal [Levene and Meyer, 1927] was acetylated in the usual way with pyridine and acetic anhydride at room temperature. The oil which separated when the acetylation mixture was poured into water crystallised without much difficulty. From aqueous alcohol it crystallised as clumps of stout prisms, frequently pointed at one end; m.p. $51-52^\circ$; $[\alpha]_D^{17} + 31.2^\circ$. Yield 80–90 %.

2 g. of this product gave 1.4 g. of heptaacetyl-*d*-mannose when acetylated for 24 hours at 38° with a mixture of 20 ml. acetic anhydride and 1 ml. H_2SO_4 . The substance crystallised in stout needles from dilute alcohol and melted, when thoroughly dried, at 122° . In chloroform solution $[\alpha]_D$ is $+0.4^\circ$ and, as in other cases, the mannose isolated after hydrolysis had the normal rotation. (Found: C, 49.05; H, 5.93; acetyl, 62.0 %. Calculated for $\text{C}_{18}\text{H}_{28}\text{O}_{14}$: C, 48.76; H, 5.73; acetyl, 61.2 %.)

Heptaacetyl-d-glucose.

Pentaacetyl-*d*-glucose diethylmercaptopal [Wolfrom, 1929] can be acetylated under exactly the same conditions as the corresponding galactose derivative and, by the same process of isolation, gives rise to a somewhat larger amount of heptaacetylglucose, *e.g.* from 5 g. of non-crystalline pentaacetylglucose mercaptopal 2.5 g. of heptaacetylglucose can be prepared. It can be recrystallised from methyl alcohol, ethyl alcohol or water but it is difficult to remove every trace of solvent from the crystals. m.p. $121-2^\circ$; $[\alpha]_D^{19} + 7.9^\circ$ in chloroform. Glucose having the normal optical rotation was isolated from this after acid hydrolysis. (Found: C, 49.34; H, 5.94; acetyl, 63.0 %. Calculated: C, 48.76; H, 5.73; acetyl, 61.2 %.)

Hexaacetyl-l-arabinose.

Tetraacetyl-*l*-arabinose diethylmercaptopal (2 g.) [Wolfrom and Newlin, 1930] when acetylated in the usual way with 1 part H_2SO_4 to 20 of acetic anhydride gave 0.93 g. of the hexaacetate. This crystallises from dilute alcohol as sheaves of fine needles; m.p. 91° ; $[\alpha]_D^{17} - 27.7^\circ$ in chloroform. (Found: C, 48.95; H, 5.72; acetyl, 62.1 %. Calculated for $\text{C}_{17}\text{H}_{24}\text{O}_{12}$: C, 48.56; H, 5.76; acetyl, 61.4 %.)

Hexaacetyl-l-rhamnose.

l-Rhamnose diethylmercaptopal [Fischer, 1894] was acetylated with pyridine and acetic anhydride and the product recrystallised from dilute alcohol. It crystallises in thin hexagonal plates; m.p. 60° ; $[\alpha]_D^{15} + 39.5^\circ$ in chloroform.

When acetylated with acetic anhydride and sulphuric acid this material gives a 67 % yield of hexaacetyl-*l*-rhamnose. This crystallises as clusters of fragile plates from aqueous methyl alcohol; m.p. $72-3^\circ$; $[\alpha]_D^{17} - 7.5^\circ$ in methyl alcohol. (Found: C, 49.92; H, 6.05; acetyl, 59.4 %. Calculated for $\text{C}_{18}\text{H}_{26}\text{O}_{12}$: C, 49.75; H, 6.03; acetyl, 59.44 %.)

Hexaacetyl-d-xylose.

Hexaacetyl-*d*-xylose has not yet been obtained crystalline but a pale yellow gum with the properties that would be expected for such a substance can be

isolated by the usual method from the products of the acetylation of tetraacetyl-*d*-xylose diethylmercaptal [Wolfrom *et al.* 1931]. This gum contains 59 % of acetyl and in chloroform solution has $[\alpha]_D^{17} + 4.0^\circ$.

SUMMARY.

By the acetylation of pentaacetyl-*d*-galactose diethylmercaptal with acetic anhydride in the presence of sulphuric acid, heptaacetyl-*dl*-galactose has been prepared.

By the same method heptaacetyl derivatives of *d*-glucose and *d*-mannose and hexaacetyl derivatives of *l*-arabinose, *l*-rhamnose and *d*-xylose have been prepared for the first time.

The preparation and properties of pentaacetyl-*d*-mannose diethylmercaptal, and tetraacetyl-*l*-rhamnose diethylmercaptal are described.

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