g.). Recrystallization from methanol gave methyl 2,3,4,6-tetra-*O*-acetyl β-D-glucopyranoside, m.p. and mixed m.p. 104–105°, $[\alpha]^{27}\text{D}$ −22.2° in ethanol (*c* 2.7); literature values: m.p. 104–105[4,12] and $[\alpha]^{20}\text{D}$ −24.6° (ethanol),[13] −27,2° (ethanol).[4]

Deacetylation of the methyl tetra-*O*-acetyl β-D-glucopyranoside by the Zemplén method[14] using catalytic amounts of sodium methoxide gave methyl β-D-glucopyranoside, m.p. and mixed m.p. 115–116°, $[\alpha]^{27}\text{D}$ −30.3° in water (*c* 2.0) (after recrystallization from methanol–ether); literature values: m.p. 110°,[15] 105°[16] and $[\alpha]^{15}\text{D}$ −32° (H_2O),[15] −34.2° (H_2O).[16]

2. **Methyl β-Lactoside.**—Application of the above procedure to acetobromo lactose yielded the corresponding methyl β-lactoside, m.p. 205°, $[\alpha]^{25}\text{D}$ +1° in water (*c* 5.0). Inasmuch as the pure methyl β-lactoside showed $[\alpha]^{25}\text{D}$ +5.6° in water[5] it is believed that the compound above contained some of the α-anomer.

B. 1. Methyl α-D-Mannopyranoside.—To crystalline D-mannose (18.0 g.) was added 3% hydrogen chloride in methanol (15 ml.) and ethylene dichloride (30 ml.). The mixture was refluxed on the water-bath for 4 hours. During the course of the reaction a two-phase liquid system was formed, the lower layer of which soon turned to a solid crystalline mass. After being allowed to cool, the reaction mixture was filtered and washed with a little ice-cold methanol followed by ether. The crystalline methyl α-D-mannopyranoside (yield 9.7 g.) had m.p. and mixed m.p. 191–192°, $[\alpha]^{20}\text{D}$ +79.0° in water (*c* 1.0) (after recrystallization from 80% ethanol); literature values: m.p. 191–192°,[17] $[\alpha]^{20}\text{D}$ +79° (H_2O),[17] +79.2° (H_2O).[18]

2. **Methyl β-L-Arabopyranoside.**—A mixture of 3% methanolic hydrogen chloride (70 ml.), ethylene dichloride (100 ml.) and L-arabinose (70 g.) was refluxed for 3 hours and allowed to stand overnight. The methyl β-L-arabopyranoside (yield 23.5 g.) was filtered off and washed with ethyl acetate and recrystallized from absolute ethanol, m.p. and mixed m.p. 166–168°, $[\alpha]^{19}\text{D}$ +235° in water (*c* 1.7); literature values: m.p. 169°[19] and 169–171°.[20]

Repeated recrystallization did not change the specific rotation which does not agree with the literature value ($[\alpha]^{20}\text{D}$ +245.5° in water).[19] As a further check on its purity a sample of the material ($[\alpha]\text{D}$ +235°) was oxidized with periodic acid according to the procedure of Hudson and Jackson.[21] The D′-methoxydiglycolic aldehyde obtained had $[\alpha]^{20}\text{D}$ +123° (H_2O); Hudson and Jackson[21] reported $[\alpha]^{20}\text{D}$ +124° (H_2O) for this substance.

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The Condensation of D-Arabinose with Nitromethane in Aqueous Solution

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The condensation of nitromethane[1] and nitroethanol[2] with aldose sugars, as a step in the preparation of higher-carbon aldoses and ketoses, has been carried out previously in dry, alcoholic media. In most successful examples of the reaction, the solubility relationships between the reactants and the alcoholic solvent were such that the alkali-sensitive sugars dissolved and the resulting salts of the nitrodeoxyalditols precipitated as the condensation reaction progressed. While many of the aldose sugars condense satisfactorily with nitromethane in alkaline alcoholic media, others such as D-glucose react to only a minor extent.[3]

With a view to increasing the scope and utility of the nitroparaffin–sugar condensation, the reaction now is being studied in *aqueous* solution. The condensation of D-arabinose with nitromethane in aqueous alkali has been found to proceed rapidly and to an extent comparable with that observed in alcoholic media.

It seems likely that the use of aqueous reaction conditions will appreciably extend the applicability of the nitromethane and related syntheses in the sugar field. Further experiments are contemplated to generalize the above results.

Experimental

Solutions containing D-arabinose in 2 equivalents of 2 *M* nitromethane in 2 *N* aqueous sodium hydroxide were allowed to stand at room temperature for varying lengths of time and the resulting *aci*-nitroalcohols then were decomposed by adding the solutions to warm (50°), aqueous sulfuric acid.[1] Following deionization and concentration, D-mannose was precipitated from the resulting solutions as the phenylhydrazone. The relationship between the duration of the condensation reaction and the yield of D-mannose phenylhydrazone was as follows: 5 min., 15.4%; 15 min., 20.6%; 25 min., 21.6%; 1 hr., 18.4%; 2 hr., 17.8%. When the amount of the alkaline nitromethane solution was varied, a condensation reaction time of 15 minutes resulted in the following yields of D-mannose phenylhydrazone: 1 equiv., 16.9%; 2 equiv., 20.6%; 3 equiv., 17.6%.

D-Mannose phenylhydrazone was characterized by conversion to the known anhydro-O-tetraacetate,[4] m.p. 123–124°, $[\alpha]^{25}\text{D}$ 12° in pyridine (*c* 3).

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Tetraacetates of D-Glucose and D-Galactose

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Helferich and Klein[2] first prepared 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose by removal of the trityl (triphenylmethyl) group from 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl-β-D-glucopyranose. The compound has proven to be very useful as an intermediate in the synthesis of disaccharides in the Königs–Knorr type reaction.[3] We wish to describe herein a new synthesis for 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose and the corresponding D-galactose derivative. This synthesis is made possible by the discovery[4] that mercuric acetate is an excellent reagent for replacing halogen in acetylated glycopyranosyl halides. The immediate precursors of the tetraace-

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