Note

A convenient method for the preparation of 2-deoxy-D-*erythro*-pentose

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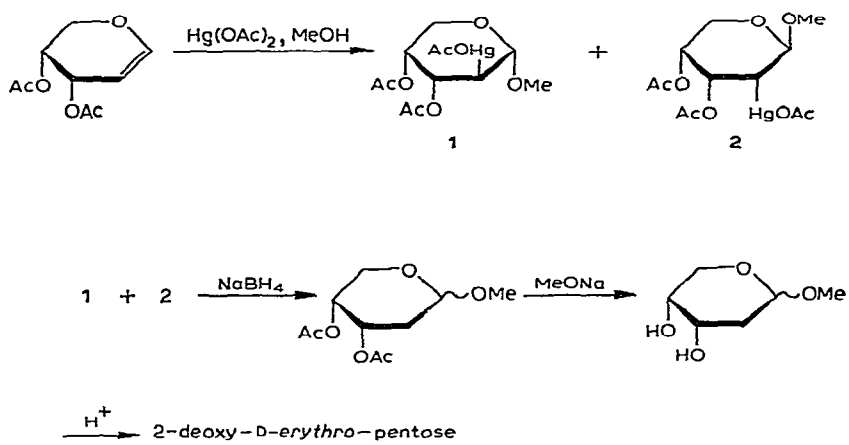
In the previous paper[1] we described the methoxymercuration of glycal acetates and reductive demercuration of the addition products with sodium borohydride, and have demonstrated that this series of reactions affords 2-deoxy sugar derivatives in high yield. The synthesis of methyl 2-deoxy-D-*arabino*-hexopyranosides by this methoxymercuration–borohydride-reduction method was reported[2] earlier. We report herein a simplified preparation of 2-deoxy-D-*erythro*-pentose by this method, starting from D-arabinal diacetate, providing a route different from the Fischer synthesis from the glycal[3].



Methoxymercuration of D-arabinal diacetate yielded two isomeric addition products, methyl 2-acetoxymercuri-3,4-di-*O*-acetyl-2-deoxy-α-D-arabinopyranoside (**1**, 35%) and methyl 2-acetoxymercuri-3,4-di-*O*-acetyl-2-deoxy-β-D-ribopyranoside (**2**, 65%) having exactly the same physical properties as the corresponding enantiomorphs[1] except that the conformational symbols and the optical signs were reversed. These mercurial adducts underwent reductive demercuration readily with sodium borohydride giving the anomeric methyl 3,4-di-*O*-acetyl-2-deoxy-D-*erythro*-pentopyranosides in exactly the same manner as described[1] for the L enantiomorphs.

The four-step synthesis was conveniently undertaken in one operation without separation or isolation of any intermediates, since both mercurial adducts gave 2-deoxy-D-*erythro*-pentose, and since all steps were rapid and quantitative. The overall yield of syrupy 2-deoxy-D-*erythro*-pentose from D-arabinal diacetate exceeded 90%. Paper-chromatographic examination of the crude product revealed contamination with a trace of a by-product, presumably D-*glycero*-pent-2-enose derived from the mercurial **1** having the α-D-*arabino* configuration. The proportion of the by-product was estimated by n.m.r. determination[1] to be ~3.5%, and this proportion could be decreased by conducting the reduction process at lower temperature.

Thus, the methoxymercuration–borohydride reduction procedure is a convenient laboratory route to 2-deoxy-D-*erythro*-pentose in excellent yield and high purity.

EXPERIMENTAL

2-Deoxy-D-erythro-*pentose from* D-*arabinal diacetate.* — Mercuric acetate (7.98 g, 25 mmoles) and D-arabinal diacetate (5.00 g, 25 mmoles) were dissolved in methanol (50 ml), and the solution was kept for 2 h. The mercurial **1** separated as crystals, which were dissolved, without isolation, by adding acetonitrile (10 ml). The solution was cooled to 0°, and sodium borohydride (100 mg) was added in small portions with continuous stirring. The precipitate of metallic mercury was filtered off, and M methanolic sodium methoxide (50 ml) was added to the filtrate. After 1 h, the solution was diluted with an equal volume of water, and deionized by passing through a column of Amberlite IR-120 (H^+, 100 ml), followed by Amberlite IRA-400 (HO^-, 100 ml). The deionized solution was evaporated to dryness to give a syrupy mixture of methyl 2-deoxy-D-*erythro*-pentosides, which was dissolved in 0.05M sulfuric acid (50 ml) and kept for 2 h at 50°. The hydrolyzate was neutralized with a saturated aqueous solution of barium hydroxide, and the precipitate of barium sulfate was centrifuged off. The supernatant was evaporated to dryness to give syrupy 2-deoxy-D-*erythro*-pentose (3.34 g, 99.6%). Although paper-chromatographic examination with Whatman No. 1 filter paper and butyl alcohol–acetic acid–water (4:1:5, upper phase, 25°) showed a faint spot of a by-product having R_G 3.58 (the hydrolyzate of methyl 2,3-didehydro-2,3-dideoxy-α-D-*glycero*-pent-2-enopyranoside obtained by deacetylation of the thiourea–demercuration product from **1** had R_G 3.59) together with the dense spot of 2-deoxy-D-*erythro*-pentose having R_G 1.94 (authentic 2-deoxy-D-*erythro*-pentose, 1.94), the product was sufficiently pure for further synthetic purposes.

Crystallization of the β-anomer was effected by inoculation of an isopropyl alcohol–acetone solution, giving a chromatographically homogeneous product, m.p. 96° (lit.[4] 96–98°); $[\alpha]_D^{28}$ −59° (*c* 1.0, water, equil.) [lit.[5] $[\alpha]_D^{17}$ −58° (*c* 1.65, water, equil.)].

Anal. Calc. for $C_5H_{10}O_4$: C, 44.77; H, 7.52. Found: C, 44.23; H, 7.69.

A portion of the syrupy crude product was dissolved in ethanol and an equi-

valent amount of aniline was added. Upon standing the crystalline aniline derivative separated, m.p. 172–173° (lit.[5] 174–175°); $[\alpha]_D^{26}$ +20.6° (*c* 1.0, methanol) [lit.[5] $[\alpha]_D^{22}$ +19.5° (*c* 1, ethanol)].

Anal. Calc. for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.19; H, 6.98; N, 6.48.

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