Total Synthesis of DL-Glucose, 3-*O*-Methyl-DL-glucose, and 3-Deoxy-DL-*ribo*-hexopyranose from 1,6:3,4-Dianhydro-β-DL-*allo*-hexopyranose, a Product Obtained from Acrolein Dimer

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The reaction of butyllithium in ether with 1,6:2,3-dianhydro-4-deoxy-β-DL-*ribo*-hexopyranose (**1**), a substance obtained in five steps from acrolein dimer, gave 1,6-anhydro-3,4-dideoxy-β-DL-*erythro*-hex-3-enopyranose (**2**). The compound 1,6:3,4-dianhydro-β-DL-*allo*-hexopyranose (**3**), obtained from **2**, was converted by reaction with aqueous barium hydroxide followed by hydrolysis of the product, to DL-glucose **5**. Treatment of **3** with sodium methoxide in methanol followed by acid hydrolysis of the 1,6-anhydro intermediate **6**, gave 3-*O*-methyl-DL-glucose (**7**). The same intermediate, **6**, along with the methyl glycoside **8**, could be obtained by the acid-catalyzed reaction of **3** with methanol. Lithium aluminum hydride reacted with **3** to form 1,6-anhydro-3-deoxy-β-DL-*ribo*-hexopyranose (**9**), which was hydrolyzed readily to 3-deoxy-DL-*ribo*-hexopyranose (**10**).

Yields were excellent throughout. All products obtained from the oxirane **3** were those resulting only from *trans* diaxial opening of the oxirane ring.

La réaction du butyllithium dans l'éther avec le 1,6:2,3-dianhydro-4-déoxy-β-DL-*ribo*-hexopyranose (**1**), une substance obtenue en cinq étapes à partir du dimère de l'acroléine, a donné le 1,6-anhydro-3,4 didéoxy-β-DL-*erythro*-hex-3-énopyranose (2). On a converti le composé 1,6:3,4-dianhydro-β-DL-*allo*-hexopyranose (**3**), obtenu de **2**, en DL-glucose **5**. par la réaction avec l'hydroxyde de baryum en solution aqueuse suivie de l'hydrolyse du produit. Le 3-*O*-méthyl-DL-glucose (**7**) fut obtenu à partir de la réaction de **3** avec le méthoxyde de sodium dans le méthanol, suivie par l'hydrolyse acide de l'intermédiaire 1,6-anhydro **6**. On a pu obtenir le même intermédiaire **6**, avec le glycoside de méthyl **8**, par la réaction catalysée par les acides de **3** dans le méthanol. L'hydrure de lithium et d'aluminium a réagi avec **3** pour former le 1,6-anhydro-3-déoxy-β-DL-*ribo*-hexopyranose (**9**), qu'on a hydrolysé facilement en 3-déoxy-DL-*ribo*-hexopyranose (**10**).

Les rendements se sont avérés partout excellents. Tous les produits obtenus à partir de l'oxirane **3** étaient ceux résultant de l'ouverture *trans* diaxiale du noyau oxirane.

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Introduction

A preliminary communication (1) from this laboratory reported the synthesis of DL-glucose from 1,6:2,3-dianhydro-4-deoxy-β-DL-*ribo*-hexopyranose (**1**), an intermediate product obtained in five steps from acrolein dimer. This note provides the experimental details for the synthesis of DL-glucose, and as well describes the conversion of **1** to 3-deoxy-DL-*ribo*-hexopyranose and to 3-*O*-methyl-DL-glucose and its methyl glycoside, thus indicating the synthetic utility of compound **1**.

Results and Discussion

The sequence of reactions and the compounds obtained are shown in Scheme 1. The 100 MHz p.m.r. spectra obtained for all of the isolated compounds are in full agreement with the structures shown. The signals for most of the protons could be determined by spin decoupling, and these provided observed couplings which clearly supported these structures and the conformations indicated.

The reaction of *n*-butyllithium readily converted **1**, in ether, to 1,6-anhydro-3,4-dideoxy-β-DL-*erythro*-hex-3-enopyranose (**2**) whose *O*-methyl and *O*-acetyl derivatives have been described elsewhere (2). The reaction of *m*-chloroperoxybenzoic acid with **2** gave only the *exo* oxirane, **3**, as expected (3), with no evidence for simultaneous formation, even in small amount, of the *endo* oxirane isomer. Opening of the oxirane ring by base gave 1,6-anhydro-β-DL-*gluco*-hexopyranose (**4**, R = H), in good yield, and this product was hydrolyzed to DL-glucose (**5**, R = H), a crystalline solid. The 100 MHz p.m.r. spectra of **5** (R = H) in D_2O and of its pentaacetate in $CDCl_3$ were identical

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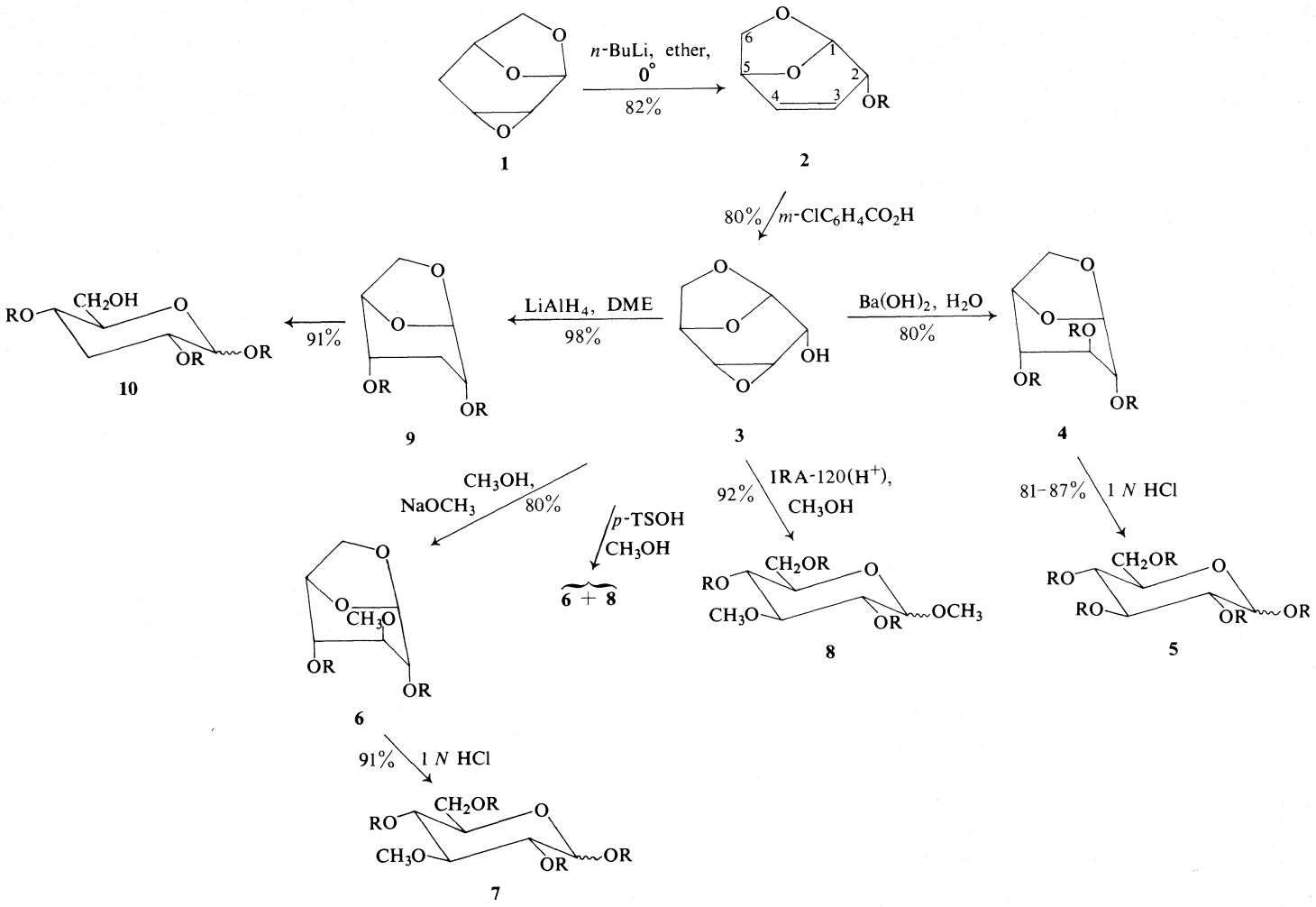

SCHEME 1

to those of authentic D-glucose and its penta-acetate.

The oxirane **3**, treated with sodium methoxide in methanol, gave a very good yield of 1,6-anhydro-3-*O*-methyl-β-DL-*gluco*-hexopyranose (**6**, R = H), a viscous oil, as the only isolable product. The p.m.r. spectra of **6** (R = H) and of its diacetate (also a viscous oil) were in accord with the assigned structures. Hydrolysis of the diacetate of **6** with 1 *N* hydrochloric acid gave an excellent yield of 3-*O*-methyl-α,β-DL-glucopyranose (**7**, R = H) whose 100 MHz p.m.r. spectrum in D_2O was identical to that of authentic 3-*O*-methyl-α,β-D-glucopyranose. Compound **6** (R = H) was also obtained as the major product when **3** was heated in methanol containing *p*-toluenesulfonic acid monohydrate. This was accompanied by the product **8** (R = H) whose formation could not be avoided. Treatment of **3** with a mixture of methanol and Amberlite IRA-120 (H^+) gave an excellent yield of what is believed to be methyl 3-*O*-methyl-α,β-DL-glucopyranoside (**8**, R = H). The 100 MHz p.m.r. spectrum of **8** (R = H) in D_2O showed two doublets ($J \sim 3.5$ and 8 Hz) in the anomeric proton region, corresponding to a mixture of the α- and β-pyranose isomers, the latter being present to the extent of ~5–10%. All the signals of the D_2O p.m.r. spectrum of authentic methyl 3-*O*-methyl-α-D-glucopyranoside (in which the anomeric proton signal for the β-isomer was absent) were found in the spectrum of the DL-glucopyranoside. However, there were additional signals present in the spectrum of the DL-glucopyranoside, but these could be due to the presence of the contaminating β-isomer. Better corroboration of the structure of **8** was found when it was converted to a crystalline triacetate, whose 100 MHz p.m.r. spectrum in $CDCl_3$ was identical to that of the triacetate of authentic methyl 3-*O*-methyl-α-D-glucopyranoside.

Treatment of a solution of **3** in tetrahydrofuran (THF) with $LiAlH_4$ gave a nearly quantitative yield of 1,6-anhydro-3-deoxy-β-DL-*ribo*-hexopyranose (**9**, R = H). Acid-catalyzed hydrolysis of **9** (R = H) gave **10** (R = H) whose p.m.r. spectrum in D_2O possessed four sets of doublets in the anomeric proton signal region, indicating that **10** (R = H) in D_2O existed as an equilibrium mixture of α- and β-pyranose and furanose structures, with the β-pyranose isomer as the major component. Acetylation of **10** (R = H) gave an excellent yield of a solid tetraacetate whose 100 MHz p.m.r. spectrum identified the structure as 1,2,4,6-tetra-*O*-acetyl-3-deoxy-β-DL-*ribo*-hexopyranose.

It is interesting that the only isolable products obtained from the reaction of **3** with each of the reagents, aqueous base, sodium methoxide in methanol, methanol containing an acid, and $LiAlH_4$ in THF, were those arising from a *trans* diaxial opening of the oxirane ring, a reaction course which has been found to take place preferentially with other oxiranes (3–6).

Experimental

Melting points and boiling points are uncorrected. Elemental analyses were made by Mrs. D. Mahlow and Mrs. A. Dunn of our microanalytical laboratory. The i.r. absorption spectra were obtained by Mr. R. Swindlehurst, of this Department, using a Perkin–Elmer Model 421 spectrophotometer. The 100 MHz p.m.r. spectra and spin decoupling experiments were made by Mr. G. Bigham and associates in this Department. Tetramethylsilane was the internal reference. Signal assignments were made with the aid of double irradiation spin decoupling. The reported coupling constants were estimated from the signal spacings where possible, and are therefore approximate values.

Column and thin layer chromatography was carried out using Silica Gel G (Merck and Co.) as adsorbent. Solvents were usually removed by rotary evaporator under vacuum, unless otherwise stated. The drying agent employed for organic solutions was anhydrous sodium sulfate.

*1,6-Anhydro-3,4-dideoxy-β-DL-erythro-hex-3-enopyranose (**2**, R = H)*

A solution of 2.56 g (0.02 mol) of the oxirane **1** (7) in 50 ml of anhydrous ether, was kept at 0° while 12 ml of a 22% solution of *n*-butyllithium (0.041 mol) in hexane was added dropwise over a 15 min period. Throughout the reaction the solutions were protected from the atmosphere by nitrogen. The yellow reaction mixture was allowed to warm slowly to room temperature and then left overnight. It was treated cautiously with water and the ether layer was then separated. The aqueous layer was extracted continuously for 24 h with dichloromethane. The combined ether layer and dichloromethane extracts were dried and freed from drying agent and solvent. The resulting yellow oil solidified when cooled, and gave after crystallization from chloroform–hexane, 2.10 g (82%) of **2** (R = H), m.p. 67–68°.

Anal. Calcd. for $C_6H_8O_3$: C, 56.25; H, 6.25. Found: C, 56.31; H, 6.60.

The i.r. spectrum in chloroform showed strong absorption at 3575 (sharp) and 3445 cm^{-1} (broad) for OH.

The 100 MHz p.m.r. spectrum in $CDCl_3$ had signals at τ 4.34 for H-1 (narrow triplet, $J_{1,2} \sim 2.0$, $J_{1,3} \sim 1.5$ Hz); 6.27–6.50 for H-2, (min.)-6_{exo} and (min.)-6_{endo} (multiplet); 4.26 for H-3 (doublet of quartets), $J_{2,3} \sim$

3.5, $J_{3,4} \sim 10.0$ Hz); 3.88 for H-4 (doublet of doublets, $J_{4,5} \sim 4.5$ Hz); 5.25–5.45 for H-5 (multiplet); 6.82 for O*H* (singlet, $w/2 \sim 6$ Hz).

*1,6:3,4-Dianhydro-β-*DL*-allo-hexopyranose (**3**)*

To a solution of 2.56 g (0.02 mol) of **2** (R = H) in 100 ml of dry dichloromethane was added 6.88 g (0.04 mol) of 80% *m*-chloroperoxybenzoic acid. The reaction mixture was protected from moisture while being stirred at room temperature for 24 h. The precipitated *m*-chlorobenzoic acid was removed and the filtrate stirred with excess anhydrous sodium carbonate. The solids were then removed by filtration and the filtrate freed of solvent. The crude **3**, contaminated with *m*-chlorobenzoic acid, was purified by chromatography using dichloromethane – ethyl acetate (2:1) as eluent. The first fraction contained the *m*-chlorobenzoic acid; the second contained **3** which gave colorless needles from dichloromethane – *n*-hexane, m.p. 108–109°; yield, 2.31 g (80%).

Anal. Calcd. for $C_6H_8O_4$: C, 50.00; H, 5.59. Found: C, 49.79; H, 5.25.

The i.r. spectrum in chloroform showed bands at 3515 (OH) and 1250 cm^{-1} (oxirane).

The 100 MHz p.m.r. spectrum in $CDCl_3$ showed signals at τ 4.75 for H-1 (narrow multiplet, $J_{1,2} \sim 1.0$, $J_{1,3} \sim 2.0$ Hz); 6.39 for H-2 (quartet, $J_{2,3} \sim 4.5$, $J_{2,OH} \sim 12$ Hz); 6.65 for H-3 (triplet of quartets, $J_{3,4} \sim 4.5$, $J_{3,5} \sim 0.7$ Hz); 6.77 for H-4 (doublet of doublets, $J_{4,5} \sim 1.8$ Hz); 5.28 for H-5 (complicated doublet); 6.01 for H-6_{endo} (doublet of doublets, $J_{6exo,6endo} \sim 7.5$, $J_{5,6endo} \sim 0.7$ Hz); 6.22 for H-6_{exo} (doublet of doublets, $J_{5,6exo} \sim 4.3$ Hz); 7.14 for O*H* (doublet).

*1,6-Anhydro-β-*DL*-glucopyranose (**4**, R = H)*

The oxirane **3** (0.5 g) was heated for 15 h under nitrogen with 10% barium hydroxide in a 2:1 water–dioxane solution. The solution was then cooled, diluted with dioxane, and neutralized with carbon dioxide. The barium carbonate precipitate was removed, and the filtrate freed of solvent, leaving 450 mg (80%) of colorless syrup.

A portion of this syrup (200 mg) was treated with a mixture of 5 ml of acetic anhydride and 5 ml of pyridine at room temperature for 24 h, giving 1,6-anhydro-β-DL-glucopyranose triacetate (**4**, R = CH_3CO) as a colorless syrup, b.p. 130–131° at 0.1 mm; yield, 325 mg (91%).

Anal. Calcd. for $C_{12}H_{16}O_8$: C, 50.00; H, 5.59. Found: C, 49.78; H, 5.29.

The i.r. spectrum in chloroform showed strong absorption at 1740 cm^{-1} (C=O).

The 100 MHz p.m.r. spectrum was identical to that of authentic 1,6-anhydro-β-D-glucopyranose triacetate.

α,β-DL-*Glucose (**5**, R = H)*

A quantity (200 mg) of **4** (R = H) in 10 ml of 1 *N* aqueous hydrochloric acid was heated for 5 h in an oil bath at 100°. The mixture was cooled and neutralized with Amberlite IRA-400 ($OH^{\ominus}$) and then filtered. The filtrate was freed from solvent and the residue was freeze dried, giving a colorless glassy solid which produced needles from aqueous ethanol – ether, m.p. 113–115°; yield, 190 mg (81%). Reported m.p. of a 1:1 mixture of D- and L-glucose, 112–113.5 (8).

Anal. Calcd. for $C_6H_{12}O_6$: C, 40.00; H, 6.71. Found: C, 39.60; H, 6.64.

DL-Glucose gave the same spectral characteristics shown by D-glucose and showed the presence of two anomeric proton signals in the area ratio of 1:2 for the α and β anomers.

Hydrolysis of the triacetate of **4** as above gave α,β-DL-glucose in 87% yield.

α,β-DL-*Glucose Pentaacetate (**5**, R = CH_3CO)*

Acetylation of 50 mg of **5** (R = H) as was done for compound **4** (R = H) above, gave a viscous liquid which deposited colorless prisms from chloroform – petroleum ether, m.p. 115–117°; yield, 97 mg (90%).

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.24; H, 5.64. Found: C, 49.60; H, 5.50.

The 100 MHz p.m.r. spectrum of this material in $CDCl_3$ was identical to that of authentic fully acetylated D-glucose and showed the presence of two anomeric proton signals in the area ratio of 1:2 for the α and β anomers.

*1,6-Anhydro-3-O-methyl-β-*DL*-glucopyranose (**6**, R = H)*

A solution of 400 mg of the oxirane **3** in 30 ml of dry methanol, previously treated with 1.0 g of sodium metal, was heated under reflux, and meanwhile protected by a nitrogen atmosphere. The disappearance of **3** was followed by t.l.c. using 1% methanol in chloroform as solvent. The reaction was complete after 30 h. The solution was cooled, then neutralized with IRA-120 ($H^{\oplus}$) in methanol. The resin was removed and the filtrate freed from solvents to provide, after distillation, pure **6** (R = H) as a colorless syrup, b.p. 140–143° at 0.1 mm; yield, 380 mg (80%).

Anal. Calcd. for $C_7H_{12}O_5$: C, 47.73; H, 6.87. Found: C, 47.40; H, 6.66.

*2,4-Di-O-acetyl-1,6-anhydro-3-O-methyl-β-*DL*-glucopyranose (**6**, R = CH_3CO)*

A quantity (250 mg) of **6** (R = H) was treated with 10 ml of a 1:1 mixture of acetic anhydride and pyridine for 1 h at 60°. From this was obtained 335 mg (90%) of crude diacetate which when distilled at 100–105° at 0.1 mm gave a viscous oil.

Anal. Calcd. for $C_{11}H_{16}O_7$: C, 50.77; H, 6.20. Found: C, 51.06; H, 5.91.

The i.r. spectrum in chloroform showed strong absorption at 1735 cm^{-1} (C=O).

The 100 MHz p.m.r. spectrum in $CDCl_3$ had signals at τ 4.74 for H-1 (singlet, $w/2 \sim 3.5$, $J_{1,2} \sim 1.5$ Hz); 5.38–5.65 for H-2, (min.)-4 and (min.)-5 (multiplet, $J_{5,6endo} \sim 1.5$, $J_{5,6exo} \sim 5.5$ Hz); 6.83–6.95 for H-3 (multiplet); 6.05 for H-6_{endo} (doublet of doublets, $J_{6exo,6endo} \sim 7.5$ Hz); 6.30–6.55 for H-6_{exo} (multiplet); 6.63 for OCH_3 (singlet); 7.94 and 7.96 (singlets for two CH_3CO).

*3-O-Methyl-α,β-*DL*-glucose (**7**, R = H)*

A solution of 280 mg of **6** (R = CH_3CO) in a mixture of 10 ml of 1 *N* aqueous hydrochloric acid and 5 ml of dioxane was heated at 80° for 5 h in an oil bath. The reaction mixture was cooled and neutralized with Amberlite IRA-400 ($OH^{\ominus}$) and filtered. The solvent was removed from the filtrate and the residue was freeze-dried. The resulting colorless syrup, when crystallized from methanol–ether, gave fine hygroscopic

needles, m.p. 135–137° (shrinking at 80°); yield, 190 mg (91%). The above syrup could also be distilled at 155–157° at 0.1 mm to provide a viscous oil which crystallized when seeded.

Anal. Calcd. for $C_7H_{14}O_6$: C, 43.30; H, 7.27. Found: C, 43.31; H, 7.18.

The 100 MHz p.m.r. spectrum of **7** (R = H) in D_2O after the solution had stood 24 h to allow completion of mutarotation, was identical to that of authentic 3-*O*-methyl-α,β-D-glucose.

*Methyl 3-O-Methyl-α,β-DL-glucopyranoside (**8**, R = H)*

A solution of the oxirane, **3**, (600 mg) in 50 ml of anhydrous methanol containing 2 g of Amberlite IRA-120 ($H^{\oplus}$) was heated under reflux for 60 h. The solution was cooled, separated from the resin by filtration, and the filtrate freed from solvent. The colorless syrup so obtained (800 mg, 92%) gave a single spot on a t.l.c. plate (solvent, methanol–chloroform, 1:10), and also gave an R_f value similar to that of the corresponding authentic D compound.

The i.r. spectrum of this syrup and that of authentic methyl 3-*O*-methyl-D-glucopyranoside (both in $CHCl_3$) were identical.

The 100 MHz p.m.r. spectrum of **8** (R = H) in D_2O showed signals at τ 4.97 for H-1 of the α isomer (doublet, $J \sim 3.5$ Hz); 5.38 for H-1 of the β isomer (doublet, $J \sim 8.0$ Hz) with the α anomer in large predominance. The signal for the β isomer was absent in the spectrum of the authentic D-glucopyranoside as were several other signals found in the spectrum of the DL-substance. The origin of these extra signals is unknown, but could be due to contaminating β isomer.

Acceptable evidence for the structure was obtained by conversion of **8** (R = H) to its triacetate, isolated after work-up as a colorless syrup which crystallized from ether and petroleum ether as needles, m.p. 81–81°; yield 845 mg (87%).

Anal. Calcd. for $C_{14}H_{22}O_9$: C, 50.30; H, 6.63. Found: C, 50.30; H, 6.82.

The spectral characteristics of this triacetate were identical to those of the authentic D isomer.

*Reaction of **3** with Methanol Containing p-Toluenesulfonic Acid Monohydrate*

A solution of **3** (500 mg) in 50 ml of anhydrous methanol containing 250 mg of *p*-toluenesulfonic acid monohydrate was heated under reflux for 10 h. The disappearance of **3** during the reaction was followed by t.l.c. (solvent, ethylacetate–chloroform, 2:1). The mixture was cooled and then brought to $pH \sim 9$ with sodium methoxide. The methanol was removed and the residue was diluted with 50 ml of water and this mixture was subjected to continuous liquid–liquid extraction with chloroform for 48 h. The chloroform solution was freed from solvent and gave a syrup which showed two spots on t.l.c. (2% methanol in chloroform). The two components were separated by column chromatography. The first fraction obtained by elution with 1% methanol in chloroform gave 337 mg (60%) of material identical with product **6** (R = H). The second fraction obtained by elution with 5% methanol in chloroform gave a syrup (216 mg, 30%), which on acetylation with acetic anhydride and pyridine provided 312 mg (91%) of crystalline material, m.p. 81–82°, which was identical to the triacetate of **8** above.

*1,6-Anhydro-3-deoxy-β-DL-ribo-hexopyranose (**9**, R = H)*

A solution of 500 mg of **3** in 25 ml of dry, freshly distilled tetrahydrofuran (THF) was added slowly and dropwise to a stirred suspension of $LiAlH_4$ (400 mg) in 30 ml of dry THF at room temperature and under nitrogen. After addition was completed, the reaction mixture was stirred overnight at room temperature, and then heated to reflux for 45 min. The solution was cooled and treated with 15 ml of THF saturated with water and then with 2 ml of 15% aqueous sodium hydroxide solution. The granular precipitate was removed by filtration and the filtrate was dried. Removal of the drying agent and then the solvent gave a syrup which solidified on cooling. This material showed only one spot on t.l.c. (solvent, dichloromethane). Sublimation at 100–105° at 0.1 mm provided colorless needles, m.p. 117–119°; yield, 497 mg (98%).

Anal. Calcd. for $C_6H_{10}O_4$: C, 49.31; H, 6.90. Found: C, 49.45; H, 6.66.

The i.r. spectrum in chloroform showed absorption at 3600 and 3470 cm^{-1} (OH).

The 100 MHz p.m.r. spectrum in $CDCl_3$ showed signals at τ 4.60 for H-1 (singlet, $w/2 \sim 4$ Hz); 5.75–6.50 for H-2, (min.)-4, -6_{exo}, (min.)-6_{endo}, 20H (multiplet); 7.75–8.30 for H-3_{exo}, -3_{endo} (multiplet); 5.30–5.54 for H-5 (multiplet).

*2,4-Di-O-acetyl-1,6-anhydro-3-deoxy-β-DL-ribo-hexopyranose (**9**, R = CH_3CO)*

Treatment of 300 mg of **9** (R = H) with 10 ml of a 1:1 mixture of acetic anhydride and pyridine at 60° for 0.5 h, and the solution then left overnight at room temperature, gave a colorless solid which was sublimed at 90–95° at 0.2 mm. Colorless needles, m.p. 123–124°; yield, 357 mg (96%).

Anal. Calcd. for $C_{10}H_{14}O_6$: C, 52.19; H, 6.13. Found: C, 52.31; H, 6.11.

The i.r. spectrum in chloroform showed strong absorption at 1735 cm^{-1} (C=O).

The 100 MHz p.m.r. spectrum in $CDCl_3$ had signals at τ 4.54 for H-1 (doublet, $J_{1,2}$ 1.5 Hz); 5.20–5.45 for H-2, (min.)-4, and (min.)-5 (multiplet); 7.55–8.25 for H-3_{exo}, -3_{endo} (multiplet); 6.05–6.25 for H-6_{exo}, -6_{endo} (multiplet); 7.84 and 7.86 (two singlets for CH_3CO).

*3-Deoxy-α,β-DL-ribo-hexopyranose (**10**, R = H)*

A solution of 250 mg of **9** (R = H) in a mixture of 10 ml of 1 *N* aqueous hydrochloric acid and 5 ml of dioxane was heated at 80° for 5 h with an oil bath. The mixture was cooled and then neutralized with Amberlite IRA-400 ($OH^{\ominus}$). Removal of the solvent from the filtrate gave a residue which was freeze dried. The resulting pale yellow syrup showed only one spot on t.l.c. (solvent, 7% methanol in chloroform, or 3% methanol in ethyl acetate). Distillation at 139–145° at 0.01 mm gave **10** (R = H) as a colorless viscous oil; yield 235 mg (91%); lit. m.p. of the D isomer, 108–111° (9).

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.90; H, 7.37. Found: C, 44.27; H, 7.23.

The 100 MHz p.m.r. spectrum in D_2O, taken after the compound had been in solution 48 h, showed

signals at τ 4.72 (doublet, $J \sim 4.0$ Hz), 4.91 (doublet, $J \sim 3.5$ Hz), 5.04 (doublet, $J \sim 3.0$ Hz) and 5.47 (doublet, $J \sim 8.0$ Hz) for H-1 of the α- and β-furanose and pyranose isomers, with the β-pyranose quite predominant. No change was observed in the spectrum taken again after the solution had stood for a week.

*3-Deoxy-β-DL-ribo-hexopyranose Tetraacetate (**10**, R=CH_3CO)*

Acetylation of 150 mg of **10** (R=H) as had been done for **9** (R=H) above gave a syrup from which the tetraacetate was obtained as colorless needles from ether and hexane, m.p. 114–115°; yield, 278 mg (91%).

Anal. Calcd. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.71; H, 6.02.

The i.r. spectrum in chloroform showed strong absorption at 1745 cm^{-1} (C=O).

The 100 MHz p.m.r. spectrum in $CDCl_3$ indicated that only one compound, the β-pyranose isomer, was present. Signals occurred at τ 4.39 for H-1 (doublet, $J_{1,2} \sim 8.0$ Hz); 5.05–5.35 for H-2, (min.)-4 (multiplet); 7.30–7.55 for H-3_{endo} (multiplet); 8.10–8.60 for H-3_{exo} (multiplet); 6.10–6.40 for H-5 (multiplet); 5.75–5.95 for the two C-6 protons; 7.93, 7.97, 7.99, 8.00 (four singlets for CH_3CO).

The filtrate from the above tetraacetate provided a material which had the same i.r. spectrum and R_f value on a t.l.c. plate (solvent, chloroform) as did the tetraacetate, but the 100 MHz p.m.r. spectrum showed four doublets in the anomeric proton signal region indicating the presence of both the α- and β-furanose and -pyranose isomers with the β-pyranose isomer predominant; τ 3.70 (d, $J \sim 4.0$ Hz), 3.84 (d, $J \sim 3.80$ Hz); 3.90 ($J \sim 0$ Hz) and 4.36 (d, $J \sim 8.0$ Hz).

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