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Synthesis and Chemistry of 4-Amino-4,6-dideoxy Sugars. VI. Methyl 4-Amino-4,6-dideoxy-α-D-idopyranoside[1,2]

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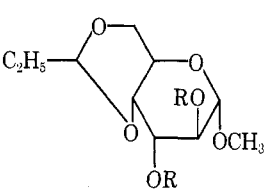
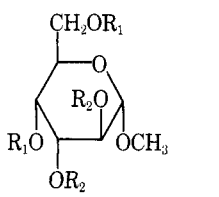
The synthesis of methyl 4-amino-4,6-dideoxy-α-D-idopyranoside (**11**) starting from methyl 4,6-*O*-benzylidene-α-D-altropyranoside (**1**) is presented. The structure of **11** was confirmed by mass spectral analysis and also by degradation of its *N*-acetate **12** to L-threoninol. Methyl 4-acetamido-2,3-di-*O*-acetyl-4,6-dideoxy-α-D-idopyranoside (**12**) is shown to exist in the *C1* conformation (**15**) in solution by NMR. The preparation of methyl 4,6-dideoxy-4-*N*,*N*-dimethylamino-α-D-idopyranoside is also discussed.

The synthesis of several 4-amino-4,6-dideoxy hexoses and their derivatives of potential biological activity were reported previously.[1,4] The preparation of the derivatives of all the eight members of this class of carbohydrates was undertaken in our laboratory with two major objectives in mind: (1) to establish the structures of those 4-amino-4,6-dideoxy hexoses such as glucose,[5] galactose,[6] and mannose,[7] which were isolated from natural sources and to provide samples for the identification of other members of these amino sugars and their derivatives which may subsequently be found to occur in nature and (2) to investigate their immunochemical and other biological properties. This paper describes the synthesis of the derivatives of 4-amino-4,6-dideoxy-D-idose.

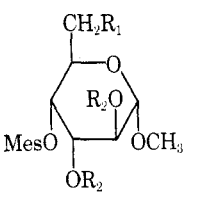
Conversion of methyl 4,6-*O*-benzylidene-α-D-altropyranoside (**1**) to its dibenzyl ether, **2**, followed by mild acid hydrolysis provided methyl 2,3-di-*O*-benzyl-α-D-altropyranoside (**3**). Treatment of **3** with excess of methanesulfonyl chloride in pyridine gave the di-*O*-methylsulfonate **4**. Selective displacement of the primary methylsulfonyl group with iodide to give **5** and subsequent reduction with Raney nickel yielded the 6-deoxy derivative, **6**. Treatment of **6** with lithium azide in dimethylformamide at 150° provided the 4-azido sugar, **7**, with inversion of configuration at C-4. Reduction of **7** with lithium aluminum hydride gave methyl 4-amino-4,6-dideoxy-2,3-di-*O*-benzyl-α-D-idopyranoside (**8**), which was characterized as its *N*-acetate, **9**. Reductive debenzylation of **9** in the presence of 10% Pd/C as a catalyst under neutral conditions gave 70% of methyl 4-acetamido-4,6-dideoxy-α-D-idopyranoside (**10**). Hydrolysis of **10** with barium hydroxide provided methyl 4-amino-4,6-dideoxy-α-D-idopyranoside (**11**) in 84% yield. Hydrogenation of **8** in the presence of 10% Pd/C and hydrogen chloride as catalysts also yielded amino sugar **11**, which was further characterized by acetylation with acetic anhydride in pyridine to obtain the triacetate **12**.



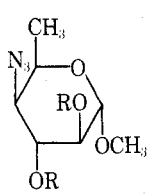
1, R = H
2, R = $CH_2C_6H_5$



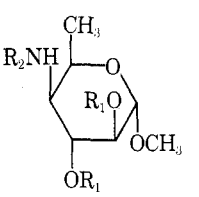
3, R_1 = H; R_2 = $CH_2C_6H_5$
4, R_1 = Mes; R_2 = $CH_2C_6H_5$



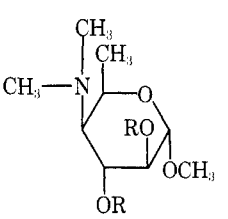
5, R_1 = I; R_2 = $CH_2C_6H_5$
6, R_1 = H; R_2 = $CH_2C_6H_5$



7, R = $CH_2C_6H_5$



8, R_1 = $CH_2C_6H_5$; R_2 = H
9, R_1 = $CH_2C_6H_5$; R_2 = Ac
10, R_1 = H; R_2 = Ac
11, R_1 = R_2 = H
12, R_1 = R_2 = Ac



13, R = $CH_2C_6H_5$
14, R = H

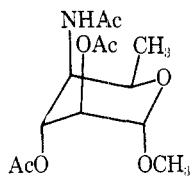
Since 4-*N*,*N*-dimethylamino-4,6-dideoxy-D-glucose oc-

curs in nature as a component of the antibiotic amicetin,[5b,10] the dimethylamino analog of 11 was prepared as follows. Treatment of 8 with formaldehyde in the presence of formic acid gave the dimethylamino derivative, **13**, as an oil which on hydrogenolysis in the presence of 10% Pd/C and HCl as catalysts provided methyl 4-*N*,*N*-dimethylamino-4,6-dideoxy-α-D-idopyranoside (**14**).

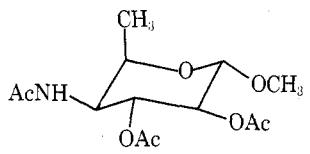
The structural assignment for the amino sugars described above is based on previous experience[4a,b] that azide displacement of the methanesulfonyl group usually occurs with inversion of configuration and without carbon skeleton rearrangement. However, formation of a 5-azido furanose by the azide displacement of a pyranose-4-methylsulfonate has also been reported.[11] The structure of **10** was therefore confirmed by the following methods.

Comparison of the mass spectra of several methyl 4-acetamido-4,6-dideoxy hexopyranosides showed that they exhibit nearly identical fragmentation patterns with only slight variations in relative intensities.[12,13] On the other hand, similar 5-acetamido sugar derivatives produce a significantly different fragmentation pattern in their mass spectra.[11,14] A mass spectrum of **10** clearly showed that it belonged to the 4-amino-4,6-dideoxy hexose series as it had an intense *m/e* peak at 74 $[CH_3CH(OH)CH(NH_2)]^+$, characteristic of a 4-acetamido-4,6-dideoxy sugar derivative.[12] In addition, degradation of **10** to L-threoninol by a previously described procedure[4d,15] confirmed the D-threo stereochemistry at C-4 and C-5 as required for a D-idose derivative.

An NMR spectrum of methyl 4-acetamido-2,3-di-*O*-acetyl-4,6-dideoxy-α-D-idopyranoside (**12**) in $CDCl_3$ indicates that this idose derivative exists as the *C1* (D) conformer, **15**



15 (*C1*)



16 (*1C*)

(*CA* in the Isbell–Tipson system of conformational nomenclature[16] and ^4C_I, according to the new British–U.S. rules[17]). Although this requires four of the five substituents to exist in the axial orientation and only the methyl (6-deoxy) group in the equatorial position, similar behavior was also observed by Horton and coworkers in the case of α-D-iodpyranose pentaacetate.[18] The NMR spectrum of **12** in $CDCl_3$ exhibited a singlet at τ 5.4 for the anomeric proton resonance, ruling out a *1C* conformation[16] **16** which would require a 1,2-diaxial coupling.[19] The other peaks in the NMR spectrum of **12** are also consistent with the above interpretation. The anomeric proton resonance in the NMR spectrum of **10** in CD_3OD also appeared at τ 5.4.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Thin layer chromatography was carried out using silica gel H from Brinkmann Instruments on 5 × 20 glass plates. A solvent system consisting of diethyl ketone, diisopropyl ketone, and ligroin (6:3:1) was used unless otherwise mentioned. The NMR spectra were taken on a Varian A-60 or T-60 spectrometer using tetramethylsilane as an internal standard. Infrared spectra were recorded on either a Beckman IR-4 or a Perkin-Elmer Infracord instrument. Specific rotations were measured using a Perkin-Elmer 141 polarimeter. The pK_a's were determined in 50% aqueous methanol. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-altropyranoside (2). A mechanically stirred mixture of 26.6 g (0.095 mol) of methyl 4,6-*O*-benzylidene-α-D-altropyranoside[9] (1), 110 g (2.76 mol) of powdered sodium hydroxide, and 250 ml of toluene was heated to reflux. Benzyl chloride (104 ml) was added to this refluxing mixture in four 26-ml portions at 1-hr intervals. An additional 27 g of NaOH was then added and the mixture was allowed to reflux for 1 more hr. The toluene and benzyl chloride were removed by steam distillation. The remaining mixture was cooled, and the yellow solid was filtered, washed with water, and recrystallized twice from ethanol to give 34.0 g (78%) of **2** as white needles, mp 90–91°, $[\alpha]^{26}D$ +38.1° (*c* 1.0, $CHCl_3$).

Anal. Calcd for $C_{28}H_{30}O_6$: C, 72.70; H, 6.53. Found: C, 72.56; H, 6.56.

Methyl 2,3-Di-*O*-benzyl-α-D-altropyranoside (3). Concentrated hydrochloric acid (3.0 ml) was added dropwise to a stirred solution of 11.93 g (0.024 mol) of **2** in 250 ml of CH_3OH at room temperature. Hydrolysis was complete in 1 hr as indicated by TLC. The mixture was neutralized with Na_2CO_3, and steam distilled. The residue was extracted with $CHCl_3$, dried (K_2CO_3), concentrated in vacuo, and then dried at 50° (0.5 mm presence) for 5 hr to give 9.0 g (95%) of **3** as a thick, colorless syrup, homogeneous by TLC. A portion of this material was chromatographed twice over Woelm grade III alumina using 50% ether–pentane as eluent to obtain an analytical sample, $[\alpha]^{26}D$ +71.5° (*c* 1.1, $CHCl_3$).

Anal. Calcd for $C_{21}H_{26}O_6$: C, 67.33; H, 7.00. Found: C, 67.36; H, 7.14.

Methyl 2,3-Di-*O*-benzyl-4,6-di-*O*-methylsulfonyl-α-D-altropyranoside (4). A solution of 8.63 g (0.02 mol) of **3** and 25.0 g (0.2 mol) of methanesulfonyl chloride in 100 ml of dry pyridine was allowed to stand at 25° for 24 hr. The mixture was poured onto water, extracted with $CHCl_3$, dried (Na_2SO_4), and concentrated in vacuo to a yellow syrup. Column chromatography over alumina gave a gum on elution with ether. Drying to constant weight under vacuum gave 8.7 g (70%) of **4** which was homogeneous by TLC. A small sample was rechromatographed over alumina for analysis.

Anal. Calcd for $C_{23}H_{30}O_{10}S_2$: C, 52.06; H, 5.70; S, 12.09. Found: C, 52.29; H, 5.75; S, 11.97.

Methyl 6-Deoxy-2,3-di-*O*-benzyl-4-*O*-methylsulfonyl-α-D-altropyranoside (6). A solution of 4.0 g (7.0 mmol) of **4** and 1.8 g (12.0 mmol) of sodium iodide in 40 ml of 2-butanone was heated under reflux with stirring for 11 hr. The mixture was cooled and the precipitated sodium methanesulfonate was removed by filtration. The filtrate was evaporated to dryness, and the residue was dissolved in $CHCl_3$, washed with 5% sodium thiosulfate solution, dried (Na_2SO_4), and concentrated in vacuo to yield 4.01 g (95%) of **5** as a thick syrup, which did not give satisfactory elemental analysis even after a column chromatography over alumina. To a solution of 3.81 g of this material (**5**) in 150 ml of warm ethanol was added an excess (9 teaspoons) of Raney nickel[20] with mechanical stirring. The mixture was then stirred at room temperature for 1 hr. Filtration of the catalyst followed by removal of the solvent gave a gum which crystallized on addition of cold water. It was recrystallized from 2-propanol to give 1.54 g (50%) of **6**, mp 85–86°, $[\alpha]^{25}D$ +53.9° (*c* 1.0, $CHCl_3$).

Anal. Calcd for $C_{22}H_{28}O_7S$: C, 60.53; H, 6.62; S, 7.35. Found: C, 60.73; H, 6.63; S, 7.54.

Methyl 4-Azido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-idopyranoside (7). A solution of 3.0 g (23 mmol) of **6** and 1.2 g (25 mmol) of lithium azide was heated under reflux for 5 hr, at which point a TLC analysis indicated the reaction to be complete. After cooling, the mixture was poured onto water, extracted with petroleum ether, and dried (Na_2SO_4) and the solvent was removed under vacuum. The chromatography of the residue over alumina using ether–pentane (2:8) as eluent gave 2.51 g (91%) of **7** as a clear liquid which was homogeneous by TLC. A small portion of this material was rechromatographed for analysis, $n^{26.5}D$ 1.5370, $[\alpha]^{26}D$ +17.4° (*c* 1.0, $CHCl_3$).

Anal. Calcd for $C_{21}H_{25}N_3O_4$: C, 65.77; H, 6.57; N, 10.96. Found: C, 65.79; H, 6.63; N, 11.01.

Methyl 4-Acetamido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-idopyranoside (9). A solution of 2.55 g (7.1 mmol) of **7** in 15 ml of dry dioxane was added with stirring to a suspension of 0.9 g (24 mmol) of $LiAlH_4$ in 40 ml of dioxane. The reaction mixture was heated to 80° and maintained at that temperature for 1 hr. The mixture was cooled and ethyl acetate was added to decompose the excess $LiAlH_4$. The solvents were removed under vacuum, the residue was suspended in ether, and water was added dropwise with stirring until the aluminum salts were converted into a white paste. The mixture was then repeatedly extracted with ether, dried (Na_2SO_4), and evaporated to dryness to give 2.2 g (93%) of **8** as a gum, pK_a = 7.65. This material was dissolved in 15 ml of pyridine, 5 ml of acetic anhydride was added, and the mixture was allowed to stand at

26° for 3 hr. Addition of ice water to the mixture provided a solid which was recrystallized twice from ethanol–water to give 1.45 g (59%) of **9**, mp 102–103°, $[\alpha]^{26}D$ +20.8° (*c* 1.18, EtOH).

Anal. Calcd for $C_{23}H_{29}NO_5$: C, 69.18; H, 7.32; N, 3.51. Found: C, 69.03; H, 7.34; N, 3.57.

Methyl 4-Acetamido-4,6-dideoxy-α-D-idopyranoside (10). A solution of 550 mg (1.4 mmol) of **9** in 50 ml of CH_3OH was hydrogenated in the presence of 200 mg of 10% Pd/C for 17 hr at 25°. Filtration of the catalyst followed by evaporation of the solvent under vacuum gave a solid which was recrystallized from $CHCl_3$–pentane to give 160 mg (70%) of **10**: mp 131–133°; $[\alpha]^{26}D$ +155.8° (*c* 1.0, EtOH); NMR (CD_3OD) τ 8.9 (d, $J_{5,6}$ = 8 Hz, 3, CCH_3), 8.0 (s, 3, $COCH_3$), 6.7 (s, 3, OCH_3), 5.4 (s, 1, C-1 H).

Anal. Calcd for $C_9H_{17}NO_5$: C, 49.31; H, 7.82; N, 6.39. Found: C, 49.54; H, 7.86; N, 6.52.

Degradation of 100 mg (0.455 mmol) of **10** according to a previously described procedure[4d,15] gave 18 mg (20% for four steps) of L-threoninol hydrogen oxalate, mp 188–189° dec. A mixture melting point with an authentic sample was unchanged.

Methyl 4-Amino-4,6-dideoxy-α-D-idopyranoside (11). A solution of 250 mg (1.15 mmol) of **10** and 250 mg of $Ba(OH)_2 \cdot H_2O$ in 10 ml of water was heated at 100° for 40 hr. The solution was cooled and acidified to pH 3 with H_2SO_4. The inorganic salts were filtered off and the filtrate was evaporated to dryness at 26° under vacuum. The residue was dissolved in CH_3OH and passed over a 5-ml column of Dowex-1 ($^-$OH form). The solvent was removed in vacuo and the residue was triturated with ether to give 170 mg (84%) of **11**, mp 114–116°. It was recrystallized from ethanol–ether–pentane for analysis, mp 118–119°, $[\alpha]^{24}D$ +82.2° (*c* 0.6, CH_3OH), pK_a = 7.90.

Anal. Calcd for $C_7H_{15}NO_4$: C, 47.44; H, 8.53; N, 7.82. Found: C, 47.43; H, 8.54; N, 8.06.

Compound **11** was also obtained as follows: a solution of 219 mg (0.6 mmol) of **8** in 50 ml of methanol was mixed with 4 drops of HCl and 75 mg of 10% Pd/C and hydrogenated at 25° for 12 hr. The catalyst was filtered and the filtrate was passed over Dowex-1 ($^-$OH form) to remove the acid. The solution was then passed through a 4-ml Dowex-50 (H^+) column and washed with 50 ml of methanol and the basic material was eluted with 100 ml of 6% NH_4OH in methanol. This solution was evaporated to dryness under vacuum and the residue was recrystallized from ethanol–ether–pentane to give 28 mg (30%) of **11**, mp 118–119°. a mixture melting point with the analyzed sample was unchanged.

Methyl 4-Acetamido-2,3-di-*O*-acetyl-4,6-dideoxy-α-D-idopyranoside (12). A solution of 102 mg (0.46 mmol) of **10** in 1.0 ml of pyridine was acetylated with 0.5 ml of acetic anhydride at room temperature for 15 hr. The solvents were removed in vacuo and the residue was dissolved in $CHCl_3$ and passed over 10 g of Merck acid-washed alumina. Removal of the solvent gave a gum which solidified on trituration with petroleum ether. It was recrystallized from acetone–pentane to give 119 mg (85%) of **12**: mp 97–98°; $[\alpha]^{26}D$ +65.2° (*c* 0.90, CH_3OH); NMR τ 8.9 (d, $J_{5,6}$ = 8 Hz, 3, CCH_3), 7.9 (3 s, 9, acetates), 6.65 (s, 3, OCH_3), 5.45–6.0 (m, 2, C-4 H and C-5 H), 5.4 (s, 1, C-1 H), 5.2 (broad s, 2, C-2 H and C-3 H).

Anal. Calcd for $C_{13}H_{21}NO_7$: C, 51.48; H, 6.98; N, 4.62. Found: C, 51.70; H, 7.03; N, 4.29.

Methyl 4,6-Dideoxy-4-*N*,*N*-dimethylamino-α-D-idopyranoside (14). A solution of 732 mg (4.1 mmol) of **11** in 4 ml of formic acid and 2 ml of 36% formalin was heated on a steam bath for 14 hr. The solution was evaporated to dryness, redissolved in ether, and extracted with 10 ml of 6 *N* hydrochloric acid. The acid layer was made basic with KOH and the liberated amine was extracted with ether, dried (K_2CO_3), and concentrated under vacuum to give 700 mg of impure **13** as a yellow oil, pK_a = 6.96. This material was dissolved in 100 ml of methanol and hydrogenated in the presence of 8 drops of HCl and 300 mg of 10% Pd/C for 29 hr. The catalyst was removed by filtration and the filtrate was evaporated to dryness. The residue was dissolved in ether and neutralized over Dowex-1 ($^-$OH). The solvent was removed under vacuum to give a gum which solidified on addition of petroleum ether. It was recrystallized from acetone–pentane to give 183 mg (50%) of **14**, mp 86–87°, $[\alpha]^{29}D$ +88.1° (*c* 1.2, $CHCl_3$), pK_a = 7.19.

Anal. Calcd for $C_9H_{19}NO_4$: C, 52.58; H, 9.46; N, 7.06. Found: C, 52.47; H, 9.57; N, 7.23.

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Registry No.—**1**, 5328-47-2; **2**, 33164-02-2; **3**, 33164-03-3; **4**, 55570-13-3; **5**, 55570-14-4; **6**, 53951-08-9; **7**, 55570-15-5; **8**, 55570-16-6; **9**, 55570-17-7; **10**, 55570-18-8; **11**, 55637-42-8; **12**, 55570-19-9; **13**, 55570-20-2; **14**, 55570-21-3; benzyl chloride, 25168-05-2; methanesulfonyl chloride, 124-63-0; lithium azide, 19597-69-4.

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