Among the known 4-phenylcoumarins of the Guttiferae, **1** is most closely related to mammea A/AB,[2] in which the chromanone ring is opened by a formal reduction to a 2-methylbutyryl chain. It represents only a minor constituent of *C. australianum* resins, the majority of which consists of complex dienedione acids similar to those of *C. brasiliensis* and *C. inophyllum*.[3] Further studies on these products are in progress.

Experimental Section

Isolation of 1.—Finely ground bark (140 g) of *C. australianum* FvM Vesq., from Bamaga, Queensland, Australia, was extracted with hexane in a soxhlet for 20 hr. The green extract was washed with 5% Na_2CO_3 until the base extract remained colorless. The hexane was dried, filtered, and evaporated. The resulting brown oil was boiled briefly in MeOH and the precipitate (identified as friedelin) was filtered off. The filtrate was evaporated, the residue was taken up in hot hexane, and slow cooling yielded **1** as white, fluffy crystals. Recrystallization from CH_2Cl_2–hexane yielded 28 mg (0.02%), mp 190–192°. A sample sublimed [100° (10^{-4} Torr)] for analysis gave mp 192–193.5°: uv (see Table I); $\lambda_{max}^{EtOH-OH^-}$ 286, 315, 425 nm; ir 5.82, 6.08, 6.20 μ; nmr ($CDCl_3$) τ −2.8 (s, 1), 2.67 (br s, 5), 4.03 (s, 1), 4.75 (t, J = 7 Hz, 1), 5.75 (m, $J \sim 6$, 11 Hz, 1), 6.64 (d, J = 7 Hz, 2), 7.4 (m, 1), 8.15 (br s, 3), 8.32 (br s, 3), 8.45 (d, J = 6 Hz, 3), 8.80 (d, J = 6 Hz, 3).

Anal. Calcd for $C_{25}H_{24}O_5$: C, 74.24; H, 5.98; mol wt, 404.1624. Found: C, 74.53; H, 6.14; mol wt, 404.1623.

Methyl Ether of 1 (2).—Methylation of **1** (12.2 mg) with Me_2SO_4 (50 μl) and K_2CO_3 in refluxing acetone for 3 hr followed by preparative tlc and crystallization gave **2** (2.5 mg), mp 115–117°; uv (EtOH) 270 (24,000), 330 (10,930) nm, unchanged by added base.

Anal. Calcd for $C_{26}H_{26}O_5$: mol wt, 418.178. Found: mol wt, 418.176.

Registry No.—**1**, 21824-07-7; **2**, 21876-35-7.

Acknowledgment.—We are grateful to CSIRO, Melbourne, for supplying a sample of *C. australianum*.

(8) G. H. Stout, M. M. Krahn, and G. D. Breck, *Tetrahedron Lett.*, 3285 (1968).

Some Normal Additions of Aminobenzoic Acids to Nitro-Olefinic Sugars[1,2]

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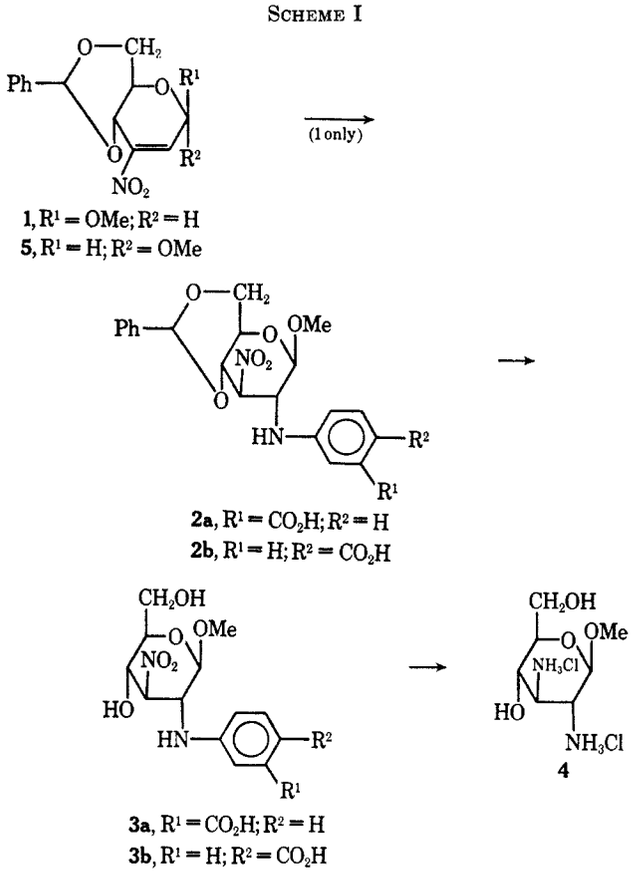
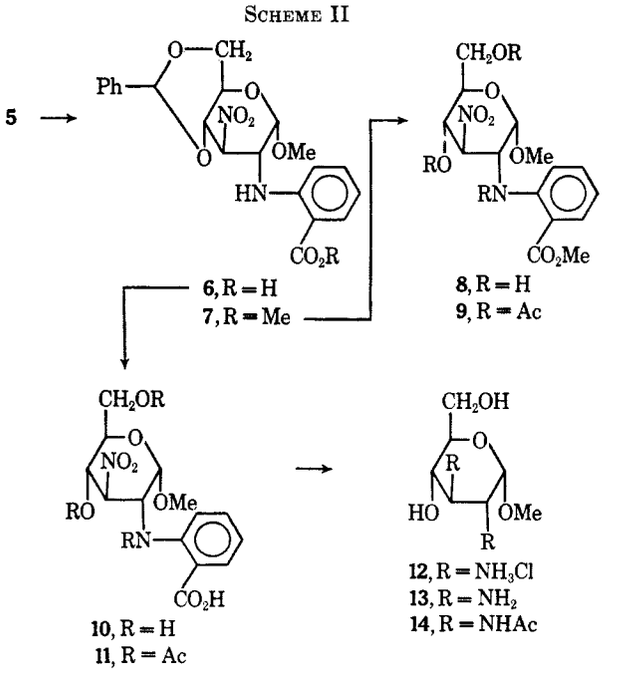
In the preceding article[1b] it was shown that nucleophilic addition of anthranilic acid to methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside (**1**) gave the expected D-*gluco* adduct (2,3-diequatorial) when excess addend and a catalytic amount of potassium hydroxide were employed. However, with equimolar proportions of anthranilic acid and **1** and no catalyst, the D-*manno* adduct was obtained in 56% yield, as *yellow* crystals. We now report the addition of the two positional isomers (*m*- and *p*-aminobenzoic acid) of anthranilic acid to the nitro olefin **1**, and also the addition of anthranilic acid to the α anomer (**5**) of **1**.

The three addition reactions, together with subsequent conversions performed in order to establish the nature of the products, are depicted in Schemes I and II.

SCHEME I



SCHEME II



In each of the systems, only the D-*gluco* adduct was obtained, regardless of the reaction conditions, and no unusual color was observed. These results suggest

(1) (a) Part XV in a series on the reactions of nitro sugars. (b) For part XIV see H. H. Baer and F. Kienzle, *J. Org. Chem.*, **34**, 3848 (1969).

(2) From the Ph.D. Theses of F. K., 1968, and F. R., 1969. Support of this work by the National Research Council of Canada is gratefully acknowledged. F. R. thanks the Council, and F. K. thanks the Ogilvie Flour Mills Co., Ltd., for the award of postgraduate fellowships.

that special factors, which are unexplained as yet, must govern the formation and solid-state color[1b] of the D-*manno* adduct from anthranilic acid and **1**.

As indicated in Scheme I, the adducts obtained from **1** and *m*- and *p*-aminobenzoic acids, namely, methyl 4,6-*O*-benzylidene-2-(3-carboxyanilino)-2,3-dideoxy-3-nitro-β-D-glucopyranoside (**2a**) and the 4-carboxyanilino isomer (**2b**), were converted by debenzylidenation (giving **3a** and **3b**, respectively) and catalytic hydrogenation into the known[1b] methyl 2,3-diamino-2,3-dideoxy-β-D-glucopyranoside dihydrochloride (**4**).

In the α-glycoside series (Scheme II), the nitro olefin (**5**) and an excess of anthranilic acid furnished 65% of methyl 4,6-*O*-benzylidene-2-(2-carboxyanilino)-2,3-dideoxy-3-nitro-α-D-glucopyranoside (**6**) when solid potassium hydroxide was used as a catalyst. A yield of 75% was obtained when the reaction was catalyzed by triethylamine. In contrast to the β series, little or no product could be isolated, even after extended reaction times, when equimolar proportions of reactants were employed and the catalyst was omitted.[3]

Compound **6** was esterified quantitatively by diazomethane. The methyl ester (**7**) was further characterized by preparation of its debenzylidenated derivative (**8**) and the *N*-acetyldi-*O*-acetyl derivative (**9**) of the latter. Debenzylidenation of the acid (**6**) gave methyl 2-(2-carboxyanilino)-2,3-dideoxy-3-nitro-α-D-glucopyranoside (**10**), which upon acetylation also yielded an *N*-acetyldi-*O*-acetyl derivative (**11**). Hydrogenation of **10** with Kuhn's catalyst[1b,4] in the presence of dilute hydrochloric acid furnished methyl 2,3-diamino-2,3-dideoxy-α-D-glucopyranoside dihydrochloride (**12**) which failed to crystallize but was characterized as the crystalline, free base (**13**) and as the di-*N*-acetyl derivative (**14**). The assignment of the D-*gluco* configuration to **6**–**14** rested upon the identification of **14** with an independently synthesized compound that was correlated chemically[5] with the known 2,3-diamino-2,3-dideoxy-D-glucose. Moreover, the nmr signals given by the pyranoside ring protons in the acetylated nitro compounds **9** and **11** could be readily analyzed and conclusively proved the α-D-*gluco* configuration. Thus, **11** showed clearly separated, one-proton signals of H-1 (doublet), H-2 (quartet), H-3 (quartet), H-4 (symmetrical triplet), and H-5 (multiplet). Their coupling constants ($J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 11.5 Hz, $J_{3,4}$ = 10 Hz, and $J_{4,5}$ = 10 Hz) confirmed the known orientations of H-1, H-4, and H-5, and required H-2 and H-3 to be axial. The spectrum of **9** allowed the same conclusion, although the H-1 doublet partly overlapped the H-3 quartet. The substituent resonances of both compounds were in accord with the structures.

Experimental Section[6]

Methyl 4,6-*O*-Benzylidene-2-(3-carboxyanilino)-2,3-dideoxy-3-nitro-β-D-glucopyranoside (2a).—The nitroolefin **1**[7] (200 mg), *m*-aminobenzoic acid (200 mg), and solid KOH (about 5 mg) were refluxed in dry, reagent grade benzene (25 ml) for 5 hr. The crude product was recrystallized from 50% aqueous ethanol to give colorless **2a** (139 mg, 47%): mp 214–215° dec, unchanged after recrystallization from ethyl acetate–petroleum ether (bp 30–60°); $[\alpha]_D$ −75.0° (*c* 0.9, acetone); ir, 3400 (sharp, NH), 3300 (broad) and 2700–2500 (weak, CO_2H), 1727 with shoulder at 1705 (C=O), and 1555 (NO_2), medium bands at 1612, 1592, 1518, 755, and 705 cm^{-1} (aromatic).

Anal. Calcd for $C_{21}H_{22}N_2O_8$ (430.4): C, 58.60; H, 5.15. Found: C, 58.84; H, 5.33.

A 94% yield of **2a** was obtained when equimolar proportions of reactants were used and the KOH was omitted, mp 215° dec, undepressed on admixing the previous sample.

Methyl 4,6-*O*-Benzylidene-2-(4-carboxyanilino)-2,3-dideoxy-3-nitro-β-D-glucopyranoside (2b).—This compound was prepared similarly to **2a**, from **1** (200 mg) and *p*-aminobenzoic acid, and it was crystallized from ethanol (5 ml) and water (1–2 ml). With KOH (about 5 mg) and excess acid (200 mg) the yield was 163 mg (56%); with 1 equiv of acid (94 mg) in the absence of KOH the yield was 168 mg (57%): mp 251–252° dec, unchanged on recrystallization from ethyl acetate–petroleum ether; $[\alpha]_D$ −95.5° (*c* 0.7, acetone); ir, 3500–2600 with sharp peak at 3380 (NH, CO_2H), 1683 (C=O), and 1557 (NO_2), medium to weak bands at 1635, 1606, 775, 750, and 700 cm^{-1} (aromatic).

Anal. Calcd for $C_{21}H_{22}N_2O_8$ (430.4): C, 58.60; H, 5.15. Found: C, 58.81; H, 5.28.

Methyl 2-(4-Carboxyanilino)-2,3-dideoxy-3-nitro-β-D-glucopyranoside (3b).—Compound **2b** (110 mg) was hydrolyzed with 70% acetic acid on a steam bath for 40 min. The product (**3b**) was obtained as fine needles (38 mg, 44%) after recrystallization from aqueous ethanol: mp 195° dec; $[\alpha]_D$ −41° (*c* 0.5, ethanol); ir, 3500–2600 with sharp peak at 3380, 1690 (C=O), 1552 (NO_2), 1610 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}N_2O_8$ (342.3): C, 49.12; H, 5.30; N, 8.18. Found: C, 49.12; H, 5.47; N, 8.30.

Methyl 2,3-Diamino-2,3-dideoxy-β-D-glucopyranoside Dihydrochloride (4). A. From 3b.—Compound **3b** (60 mg) was hydrogenated over brown palladium oxyhydrate on barium sulfate (Kuhn's catalyst[4]) as described for the preparation of **4** from the 2-carboxyphenyl isomer of **3b**.[1b] The hydrogenation product (**4**) crystallized from ethanol in a yield of 28 mg (55%): $[\alpha]_D$ −41.5° (*c* 0.8, H_2O). The identification with previously obtained **4** was accomplished by comparison of the ir spectra, paper chromatographic mobilities (R_{GN} 1.17),[8] and optical rotations. Chromatographic inspection of the mother liquor revealed the presence of additional **4** and of a faster moving material (R_{GN} 1.92) which presumably resulted from incomplete hydrogenolysis.[1b]

B. From 2a.—The compound **2a** (374 mg) was debenzylidenated with 70% acetic acid in the usual manner. The resulting syrup, which was presumed to contain **3a**, failed to crystallize and was therefore hydrogenated directly. Pure **4** (69 mg, 30%) crystallized from absolute ethanol: $[\alpha]_D$ −41.6° (*c* 0.7, H_2O); R_{GN} 1.16; ir identical with that of **4** from **3b** and previous work.[1b] Paper chromatography of the mother liquor showed additional **4**, another major spot (R_{GN} 2.10), and several faint spots (R_{GN} 0.70, 0.88, 1.30, 1.75).

Methyl 4,6-*O*-Benzylidene-2-(2-carboxyanilino)-2,3-dideoxy-3-nitro-α-D-glucopyranoside (6).—The nitro olefin **5**[9] (733 mg, 2.5 mmol), anthranilic acid (685 mg, 5 mmol), and a pellet of KOH were refluxed in dry benzene (125 ml) for 3 hr. In preliminary experiments, the progress of the reaction was monitored by tlc on silica gel G with chloroform–ethyl acetate (1:1, v/v) as irrigating solvent. It was found that **1** (R_f 0.85) disappeared within 2–3 hr with concomitant formation of a nonmigrating

(3) When dried, reagent grade benzene was used as the solvent; **1** appeared to remain unchanged during 6 days of refluxing, as judged by tlc. In one run, dried benzene of undetermined purity was used and then a small amount of **6** (but no isomer) was formed within 24 hr. Possibly the solvent had contained an impurity that was catalytically active.

(4) R. Kuhn and H. J. Haas, *Angew. Chem.*, **67**, 785 (1955); *Ann.* **611**, 57 (1958).

(5) Part XVI in this series: H. H. Baer and F. Rajabalee, *Carbohyd. Res.*, in press.

(6) For general procedures, see the preceding paper.[1b]

(7) H. H. Baer and T. Neilson, *Can. J. Chem.*, **43**, 840 (1965).

(8) Speed relative to D-glucosamine hydrochloride in the Fischer–Dörfel solvent system; see footnote 26 in ref 1b.

(9) H. H. Baer and F. Kienzle, *Can. J. Chem.*, **45**, 983 (1967). Occasional failures in the preparation of **5** could be traced to insufficient drying of the reagents and/or to access of extraneous moisture. We have now found an advantage in adding small amounts of fresh Drierite at the beginning and whenever the flask was opened for the withdrawal of test samples. Reaction times of 2 days (rather than 9 days as reported) were usually sufficient when this precaution was taken.

product (6). The latter did migrate (R_f 0.7) with chloroform–methanol (1:1, v/v).

The yellow reaction solution was treated with activated charcoal and evaporated to give a yellowish white residue. Recrystallization from absolute ethanol afforded **6** (706 mg, 65%) as nearly colorless needles: mp 254–255° dec, raised to 260–261° dec by recrystallization from ethyl acetate–petroleum ether; $[\alpha]_D$ +56.9° (*c* 0.9, DMF); ir, 3360 (sharp, NH), 3240 and 2700–2500 (broad, CO_2H), 1668 (strong, C=O) and 1550 (strong, NO_2), medium bands at 1578, 1520, 773, 755, and 704 cm^{-1} (aromatic).

An essentially identical experiment in which triethylamine (2 ml) was substituted for the KOH pellet required 3.5 hr for completion. The mixture was evaporated to dryness with successive additions of toluene, ligroin, and ethanol (two portions each). Recrystallization from ethanol gave **6** (795 mg, 75%): mp 252–254° dec, raised to 261–262° by recrystallization from ethyl acetate–petroleum ether; $[\alpha]_D$ +57.1° (*c* 0.8, DMF); ir as above.

Anal. Calcd for $C_{21}H_{22}N_2O_8$ (430.4): C, 58.60; H, 5.15; N, 6.51. Found: C, 58.74; H, 5.16; N, 6.43.

Similar experiments using equimolar amounts of reactants gave in the presence of KOH, small yields (10–15%) of **6**, mp 256–257° dec, which crystallized with difficulty, and in the absence of KOH, little or no product.[3]

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2-[2-(methoxycarbonyl)anilino]-3-nitro-α-D-glucopyranoside (7).—To a cooled (0°) solution of **6** (523 mg) in tetrahydrofuran (20 ml) was added, dropwise and with stirring, a cold solution of diazomethane in ether until a slight yellow tinge persisted. The solvents were evaporated and the residue was recrystallized from ethyl acetate–petroleum ether to give white, microscopic needles of **7** (526 mg, 98%): $[\alpha]_D$ +19.3° (*c*, 1, $CHCl_3$); ir, 3330 (NH), 1690 (C=O), 1553 (NO_2), 1607, 1585, 1525, 760–750, and 704 cm^{-1}. The ester sublimed between 215 and 223° without melting.

Anal. Calcd for $C_{22}H_{24}N_2O_8$ (444.4): C, 59.45; H, 5.44; N, 6.30. Found: C, 59.66; H, 5.48; N, 6.26.

Methyl 2,3-Dideoxy-2-[2-(methoxycarbonyl)anilino]-3-nitro-α-D-glucopyranoside (8).—Compound **7** (137 mg) was heated in 70% acetic acid for 40 min on a steam bath, the reaction mixture was evaporated to dryness (with two ultimate additions of ethanol), and the white residue was recrystallized from ethyl acetate–petroleum ether to give **8** as thin needles (90 mg, 82%): dec 165–200°; $[\alpha]_D$ +68.3° (*c* 0.8, methanol); ir, 3425, 3345, 3200 (NH, OH), 1680 (C=O), 1554 (NO_2), 1600, 1590, 1528, and 760 cm^{-1}.

Anal. Calcd for $C_{15}H_{20}N_2O_8$ (356.3): C, 50.56; H, 5.66; N, 7.86. Found: C, 50.45; H, 5.79; N, 7.86.

Methyl 4,6-Di-*O*-acetyl-2,3-dideoxy-2-[*N*-(2-methoxycarbonylphenyl)]acetamido-3-nitro-α-D-glucopyranoside (9).—Compound **8** (80 mg) was suspended in acetic anhydride (2 ml), and it dissolved with evolution of heat upon addition of boron trifluoride etherate (3 drops). After standing for 1 hr at room temperature the mixture was stirred for 15 min with excess ice water. The aqueous solution was extracted with chloroform, and the extract was dried (Na_2SO_4), treated with activated charcoal, and evaporated to a syrup. The syrup yielded beautiful platelets of **9** (67 mg) by crystallization (1 day at 2–5°) from a small amount of ethyl acetate and petroleum ether: mp 71–74°; $[\alpha]_D$ +167.5° (*c* 0.2, $CHCl_3$); ir, 1750 and 1722 (ester C=O), 1668 (amide C=O), 1562 (NO_2), 762 cm^{-1} (aromatic); nmr (100 MHz, $CDCl_3$) τ 1.9–2.8 (complex multiplets, 4 aryl protons), 3.98 (q, J = 3.3 and 11.5 Hz, H-2), 4.44 (t, J = 10 Hz, H-4), 5.12 (d, J = 3.3 Hz, H-1), 5.17 (q, J = 10 and 11.5 Hz, H-3), 5.88 (m, 2 H, H-6,6′), 6.14 (s, 3 H, CO_2CH_3), 6.25 (m, H-5), 7.06 (s, 3 H, OCH_3), 7.93 and 8.00 (s, 6 H, 2 OAc), 8.31 (s, 3 H, NAc).

The compound contained chloroform of crystallization. This was evident from the mass spectrum ($CHCl_2^+$ fragments at *m/e* 83, 85, and 87 in the ratio 9:6:1) and from a noticeable enhancement of the small nmr signal (τ 2.77) normally present in $CDCl_3$. Microanalytical data fitted the presence of 0.75 mol of $CHCl_3$.

Anal. Calcd for $C_{21}H_{26}N_2O_{11}$ (482.4): C, 52.28; H, 5.43; N, 5.81. Calcd for $C_{21}H_{26}N_2O_{11} \cdot {}^3/_4CHCl_3$ (572.0): C, 45.67; H, 4.71; N, 4.90. Found: C, 45.67; H, 4.81; N, 4.71.

Methyl 2-(2-Carboxyanilino)-2,3-dideoxy-3-nitro-α-D-glucopyranoside (10).—Compound **6** (386 mg) was debenzylidenated as described for the preparation of **8** from **7**. The crude product (273 mg, mp 189–190° dec) was treated with activated charcoal in ethyl acetate and recrystallized by adding petroleum ether to give pure **10** (203 mg, 67%) as small, stout prisms: mp 204–205° dec, $[\alpha]_D$ +80.8° (*c* 1, methanol); ir, 3450–3150 (NH, OH), 2700–2500 (weak, CO_2H), 1655 (C=O), 1555 (NO_2), 770 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}N_2O_8$ (342.3): C, 49.12; H, 5.30; N, 8.18. Found: C, 49.21; H, 5.46; N, 8.06.

Methyl 4,6-Di-*O*-acetyl-2-[*N*-(2-carboxyphenyl)]acetamido-2,3-dideoxy-3-nitro-α-D-glucopyranoside (11).—The compound **10** (108 mg) was acetylated with acetic anhydride (3 ml) and BF_3–etherate (3 drops) as described for the acetylation of **8**. The dried chloroform extract was evaporated, and the residue crystallized after three evaporations with ethanol. Recrystallization from ethyl acetate–petroleum ether gave **11** as white platelets (91 mg, 62%): mp 199–200° dec; $[\alpha]_D$ +189° (*c* 0.9, $CHCl_3$); ir, 2600–2500 (weak, CO_2H), 1766, 1743 (ester C=O), 1700 (acid C=O), 1625 (amide C=O), 1562 (NO_2), 755 cm^{-1}; nmr (100 MHz, $CDCl_3$) τ 1.6 (broad signal, 1 H, CO_2H), 1.85–2.85 (complex multiplets, 4 aryl protons), 4.00 (q, J = 3.5 and 11.5 Hz, H-2), 4.43 (t, J = 10 Hz, H-4), 4.93 (d, J = 3.5 Hz, H-1), 5.15 (q, J = 10 and 11.5 Hz, H-3), 5.86 (m, 2 H, H-6,6′), 6.25 (m, H-5), 6.96 (s, 3 H, OCH_3), 7.92 and 7.97 (s, 6 H, 2 OAc), 8.23 (s, 3 H, NAc).

Anal. Calcd for $C_{20}H_{24}N_2O_{11}$ (468.4): C, 51.29; H, 5.16; N, 5.98. Found: C, 51.51; H, 5.31; N, 5.82.

Catalytic Hydrogenation of 10. A. Methyl 2,3-Diamino-2,3-dideoxy-α-D-glucopyranoside (13).—A solution of **10** (900 mg) in ethanol (25 ml) and water (10 ml) was acidified with 1 *N* HCl (7 ml) and hydrogenated at ordinary temperature and pressure in the presence of Kuhn's catalyst[4] (1 g, prehydrogenated in 10 ml of water). Hydrogen uptake was rapid initially but then became slow, ceasing after 3–5 days in various runs. The reaction mixture was filtered through Celite and evaporated to give a jelly-like residue that failed to crystallize. Paper chromatography showed a main spot (R_{GN} 1.13,[8] presumably the dihydrochloride **12**) and an additional, minor spot (R_{GN} 1.99, presumably a product due to incomplete hydrogenolysis[1b]). The amorphous material was dissolved in water (10 ml) and passed through a column containing 40 ml of Dowex 1-X2 (OH^-) anion-exchange resin. The column was eluted with water (250 ml), and evaporation of the effluent followed by two coevaporations with ethanol gave a white solid. Crystallization from ethanol–ethyl acetate produced chromatographically homogeneous **13** as hexagonal prisms (227 mg, 45%): R_{GN} 1.15; mp 170–171° (darkening from 160°); $[\alpha]_D$ +147.2° (*c* 1, H_2O); ir, broad absorption in the 3000 region, with sharp peaks at 3375 and 3305 (OH, NH_2), 1590 cm^{-1} (NH bending).

Anal. Calcd for $C_7H_{16}N_2O_4$ (192.2): C, 43.74; H, 8.39; N, 14.58. Found: C, 43.82; H, 8.59; N, 14.46.

B. Methyl 2,3-Diacetamido-2,3-dideoxy-α-D-glucopyranoside (14).—A hydrogenation of **10** (838 mg) was performed as described under A. The eluate from the anion-exchange column was evaporated after neutralization with 1 *N* HCl in an effort to produce the dihydrochloride **12** in crystalline form. The amorphous but chromatographically homogeneous foam which was obtained failed to crystallize. It was then N-acetylated by stirring its solution in water (20 ml) and methanol (3 ml) with acetic anhydride (2 ml) and Dowex 1-X2 (CO_3^{2-}) (7 ml), for 2 hr at 0°.[10] The filtered solution was stirred briefly with a small amount of Rexyn 101(H^+), filtered again, and evaporated. The residue was crystallized from a very small amount of 95% ethanol by slow addition of a relatively large amount of ethyl acetate. Microscopic needles of **14** were obtained in a yield of 125 mg (20%): mp 245–246° dec, undepressed on admixing **14** from a different source;[5] $[\alpha]_D$ +60.4° (*c* 1, methanol); ir, identical with that of **14** [lit.[5] mp 245–246° dec, $[\alpha]_D$ +60.0° (*c* 0.8, methanol)].

Registry No.—**2a**, 21893-09-4; **2b**, 21893-10-7; **3b**, 21893-11-8; **6**, 21893-12-9; **7**, 21893-13-0; **8**, 21893-14-1; **9**, 21893-15-2; **10**, 21893-16-3; **11**, 21893-17-4; **13**, 21893-18-5; **14**, 21893-19-6.

(10) For a repetition it would seem recommendable to omit the preceding neutralization with HCl and to either isolate **13** (as under A) or proceed directly with *N*-acetylation of the column eluate. In the latter case no resin would be needed and a higher yield of **14** might be obtained.