4, C_6H_4), 4.88 (s, 1, 1-H; on expanded scale, $J_{1,2}$ = 0.5 Hz), 5.4 and 5.75 (5-H_2 as doublet plus singlet and 4-H as quartet of doublets), 4.20 (AB quartet resembling a triplet, 2-H and 3-H, $J_{2,3}$ = 3.5 Hz), 6.48 (s, 3, OCH_3).

Anal. Found: C, 52.4; H, 4.48.

Registry No.—**2**, 17229-98-0; **3**, 17229-99-1; **4**, 17230-00-1; **5**, 17278-14-7; **6**, 17230-01-2; **8**, 17230-02-3; **9**, 17230-03-4; **10**, 17230-04-5; **11**, 17230-05-6; **12**, 17230-06-7.

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A Novel Furanoside Synthesis. Conversion of Methyl 6-Deoxy-6-nitro-α-D-glucopyranoside into Methyl 3-Deoxy-3-nitro-β-L-ribo- and -arabinofuranosides and Corresponding Amino Sugars[1]

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A novel way of synthesizing methyl 3-amino-3-deoxypentofuranosides is described. Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-nitro-α-D-glucopyranoside (**1**) was prepared by an improved procedure and methanolized by catalysis with methyl *p*-toluenesulfonate to give crystalline methyl 6-deoxy-6-nitro-α-D-glucopyranoside (**2**). Periodic acid oxidation of **2** to dialdehyde **3** (not isolated), internal nitroalkane–aldehyde addition in the latter at pH 7.5 to a mixture of stereoisomeric methyl 5-aldo-3-deoxy-3-nitro-pentofuranosides (**4**, not isolated), and subsequent sodium borohydride reduction gave crystalline methyl 3-deoxy-3-nitro-β-L-ribofuranoside (**5**, major isomer) and methyl 3-deoxy-3-nitro-β-L-arabinofuranoside (**6**, minor isomer). The sequence constitutes a shortening of a sugar chain "from within," without chemical involvement of the glycosidic center. Catalytic hydrogenation and derivatization by standard procedures led, from **5**, to the corresponding amine hydrochloride (**7**), the amine **8**, and the acetamido derivative **9**. Acid hydrolysis of **7** gave known 3-amino-3-deoxy-L-ribose hydrochloride (**10**). A similar sequence performed with **6** gave the corresponding amino (**11**), isopropylidenamino (**12**), and acetamido (**13**) derivatives and finally, known 3-amino-3-deoxy-L-arabinose hydrochloride (**14**).

The nitromethane cyclization of "sugar dialdehydes," introduced 10 years ago[2] and often since employed for the synthesis of deoxynitro and thence aminodeoxy sugars,[3] is encumbered by a structural limitation inherent in the dialdehydes which are obtained by glycol cleavage of ordinary glycosides of both the pyranoid and the furanoid types. Ring closure by nitromethane addition leads to 3-deoxy-3-nitroaldopyranosides[2,3] (or, departing from ketosides, to 4-deoxy-4-nitroketopyranosides[4]), but nitro*furanosides* cannot be so prepared.[5] In fact, whereas some 3-amino-3-deoxyaldofuranosides have been synthesized *via* other routes,[6] no representative of an analogous group of nitro compounds is known. Interest in such 3-deoxy-3-nitroaldofuranosides appears warranted, however, and is derived mainly from two considerations. First, they would presumably be capable of reduction and thereby serve to complement existing ways of entry into the series of amino furanosides, of which some members, notably puromycin and 3′-aminoadenosine, have drawn considerable biochemical and medicinal attention. Secondly, certain further chemical properties expected to occur in 3-deoxy-3-nitroaldofuranosides should be worthy of examination. For example, one would predict these compounds to constitute yet another variety of that class of glycosides which undergo facile cleavage by alkali. It is known that 2-nitroethyl β-D-glucopyranoside[7] as well as methyl 6-deoxy-6-nitrohexopyranosides[8] suffer fission of their glycosidic bonds in alkaline medium, and with these structures the 3-deoxy-3-nitroaldofuranosides would have in common an activating nitro substituent in β position to one of the acetal oxygens.

For these and similar reasons a synthesis of nitro furanosides was sought, and it was found that methyl 6-deoxy-6-nitro-α-D-glucopyranoside may be converted into two methyl 3-deoxy-3-nitro-β-L-pentofuranosides in a simple operation based on the nitroalkane–aldehyde reaction.

Preparation of Methyl 6-Deoxy-6-nitro-α-D-glucopyranoside (**2**).—To prepare the required starting material, the 6-nitro glucoside **2**, two approaches were considered. We have recently reported[8] the methanolysis of 1,2-*O*-isopropylidene-6-deoxy-6-nitro-α-D-glucofuranose, a compound that can be synthesized without much trouble by the nitromethane method of Grosheintz and Fischer.[9] However, the methanolysis gives a syrupy, anomeric mixture of methyl 6-deoxy-6-nitro-D-glucopyranosides rather than the single ano-

(1) Part X in a series on reactions of nitro sugars. Part IX: H. H. Baer and K. S. Ong, *Can. J. Chem.*, **46**, 2511 (1968).

(2) H. H. Baer and H. O. L. Fischer, *Proc. Natl. Acad. Sci.*, **44**, 991 (1958); *J. Amer. Chem. Soc.*, **81**, 5184 (1959).

(3) For reviews, see H. H. Baer, *Tetrahedron*, **20**, *Suppl.* **1**, 263 (1964); F. W. Lichtenthaler, *Angew. Chem. Intern. Ed. Engl.*, **3**, 211 (1964).

(4) H. H. Baer, *J. Org. Chem.*, **28**, 1287 (1963); H. H. Baer and A. Ahammad, *Can. J. Chem.*, **44**, 2893 (1966); F. W. Lichtenthaler and H. K. Yahya, *Ber.*, **100**, 2389 (1967).

(5) One example has been described in which a partially blocked glycoside served to produce 3-deoxy-3-nitro glycosides containing a seven-membered (septanoside) ring: G. Baschang, *Ann.*, **663**, 167 (1963).

(6) (a) B. R. Baker, R. E. Schaub, and J. H. Williams, *J. Amer. Chem. Soc.*, **77**, (1955); (b) C. D. Anderson, L. Goodman, and B. R. Baker, *ibid.*, **80**, 5247 (1958); (c) R. E. Schaub and M. J. Weiss, *ibid.*, **80**, 4683 (1958); (d) M. J. Weiss, J. P. Joseph, H. M. Kissman, A. M. Small, R. E. Schaub, and F. J. McEvoy, *ibid.*, **81**, 4050 (1959).

(7) B. Helferich and M. Hase, *Ann.*, **554**, 261 (1943).

(8) H. H. Baer and W. Rank, *Can. J. Chem.*, **43**, 3330 (1965).

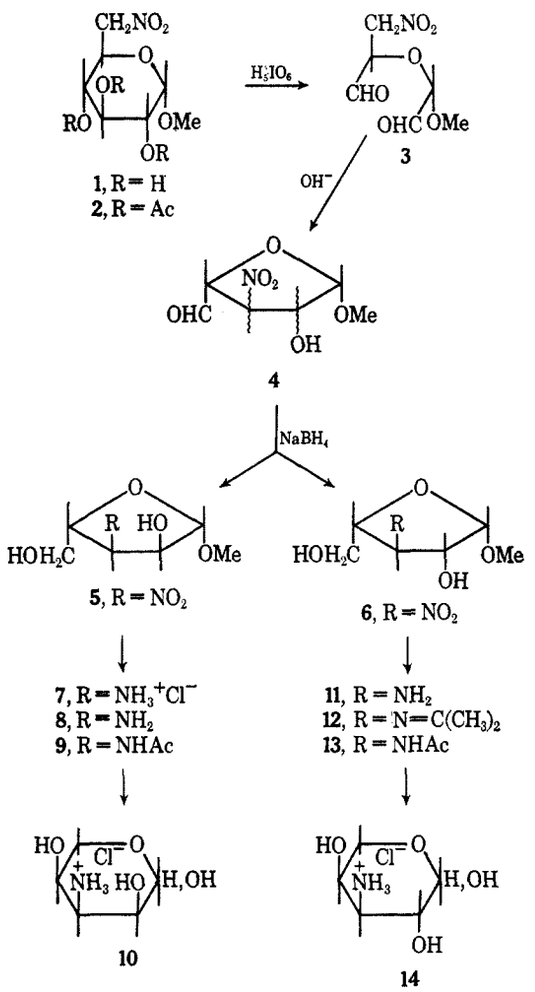
(9) J. M. Grosheintz and H. O. L. Fischer, *J. Amer. Chem. Soc.*, **70**, 1476 (1948).

mer desired for the present purpose, and fractionation of that mixture on a large scale did not appear to be an attractive project.[10] The other possibility was to introduce a nitro group by nucleophilic displacement[11] at C-6 of a suitable derivative of methyl α-D-glucopyranoside. This method was used by Sugihara, *et al.*,[12] who prepared methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-nitro-α-D-glucopyranoside (**1**), and by Lindberg,[13] who synthesized the corresponding tri-*O*-tetrahydropyranyl derivative and hydrolyzed it to produce **2**, albeit in noncrystalline condition. We have adopted the same principle and, by employing some experimental modifications, have obtained **2** in crystalline form and good yield.

Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside[14] was treated for 3 days at 16–18° with sodium nitrite in a 4:1 mixture of dimethyl sulfoxide and *N*,*N*-dimethylformamide, to give the nitro triacetate **1** in excellent yield. For the deacetylation of **1** one had to avoid alkaline conditions because of the sensitivity referred to in the introduction, and one had to refrain likewise from the use of strongly acidic conditions in order to preserve the glycosidic bond. The deacetylation was accomplished by methanolysis catalyzed by methyl *p*-toluenesulfonate, which furnished crystalline **2** in yields of 80–87%.

Conversion of 2 into Methyl 3-Deoxy-3-nitro-β-L-pentofuranosides.—The 6-nitro pyranoside **2** was oxidized with periodic acid in 95% ethanol to give the dialdehyde **3**. This dialdehyde was not isolated but, upon adjustment of its aqueous solution to pH 7.5, immediately cyclized to a mixture of stereoisomeric methyl 5-aldo-3-deoxy-3-nitropentofuranosides (**4**). The reaction could be followed by thin layer chromatography and appeared to be complete within 15 min. No attempt was made to characterize the reaction products at this stage since it was felt that nitro aldehydes of this type would be highly reactive and unstable. Rather, a borohydride reduction was performed at once and thus a product was obtained from which two crystalline, isomeric methyl 3-deoxy-3-nitropentofuranosides (**5** and **6**) were isolated in a combined yield of 26% based on **2**.

The reaction sequence represents a shortening of a sugar chain "from within,"[15] accompanied by transposition of a substituent. Inspection of the formulas shows that in going from **2** to **4** a formal interchange of ligands occurs at the carbon atom which determines the configurational series, *i.e.*, at C-5 in **2** which becomes C-4 in **4**; C-6 and C-4 of **2** appear in **4** as C-3 and C-5, respectively. Consequently, the products arising from the α-D sugar **2** possess the β-L configuration. This deduction presupposes, of course, that the penultimate carbon is not itself involved in an epimerization reaction at any stage. Such an assumption could not safely be made from the outset, as similar epimerizations have in fact been observed, although infrequently, in sugar dialdehyde–nitroalkane cyclizations.[16] However, the isolated furanosides **5** and **6** actually were revealed to be β-L compounds. The major product (mp 114–116°, $[\alpha]_D$ +32.5°) obtained by fractional crystallization was methyl 3-deoxy-3-nitro-β-L-ribofuranoside (**5**) and the minor product (mp 68–71°, $[\alpha]_D$ +128°) was methyl 3-deoxy-3-nitro-β-L-arabinofuranoside (**6**). The configurations were established by a study of the corresponding amines produced upon catalytic hydrogenation.



The Methyl 3-Amino-3-deoxy-β-L-pentofuranosides.—Hydrogenation of **5** with platinum catalyst in the presence of 1 mol of dilute hydrochloric acid furnished methyl 3-amino-3-deoxy-β-L-ribofuranoside hydrochloride (**7**) from which the free amine **8** was obtained by anion exchange. *N*-Acetylation of **8** gave the acetamido derivative **9**, and acid hydrolysis yielded known 3-amino-3-deoxy-L-ribose hydrochloride (**10**) which was identified by comparison with an authentic specimen.

(10) Upon acetylation of the mixture, the crystalline 2,3,4-tri-*O*-acetate of the α anomer was obtained in virtually pure condition, but only after lengthy fractional crystallizations which entailed poor yields.[8]

(11) N. Kornblum, *Org. Reactions*, **12**, 101 (1962).

(12) J. M. Sugihara, W. J. Teerlink, R. MacLeod, S. M. Dorrence, and C. H. Springer, *J. Org. Chem.*, **28**, 2079 (1963). Regrettably, we were not aware of this work at the time of our previous[8] study.

(13) B. Lindberg and S. Svensson, *Acta Chem. Scand.*, **21**, 299 (1967).

(14) (a) B. Helferich and W. Ost, *Z. Physiol. Chem.*, **331**, 114 (1963); (b) A. L. Raymond and E. F. Schroeder, *J. Amer. Chem. Soc.*, **70**, 2785 (1948).

(15) Conversely, the transformation of a furanoside into a pyranoside by periodate cleavage and subsequent cyclization with nitromethane constitutes a chain prolongation "from within." This principle[2] has more recently been employed in the synthesis of various nitrogenous glycosides [H. H. Baer and F. Kienzle, *Can. J. Chem.*, **43**, 3074 (1965); H. H. Baer and A. Ahammad, *ibid.*, **44**, 2893 (1966)] and in nucleoside chemistry; see ref 17.

(16) The first and seemingly unique case involved a cyclization with nitroethane: H. H. Baer and G. V. Rao, *Ann.*, **686**, 210 (1965). With nitromethane, no evidence for the occurrence of analogous epimerizations had come to light in the numerous investigations published through 1966, but recently a small amount (1.2%) of a 5-epimerized hexopyranoside derivative was isolated from mother liquors of an experiment that had yielded 53% of nonepimerized products in crystalline form: S. Inouye, *Chem. Pharm. Bull.*, **14**, 902 (1966).

TABLE I

PHYSICAL CONSTANTS OF 3-AMINO-3-DEOXY-L-PENTOSE DERIVATIVES

Compd	Found: Mp, °C	Found: $[\alpha]_D$ (H_2O), deg	Reported[a]: Mp, °C	Reported[a]: $[\alpha]_D$ (H_2O), deg	Ref
Methyl 3-amino-3-deoxy-β-L-ribofuranoside (8)	111–113	+32.7	[107–109]	[−37]	*b*
Hydrochloride (7)	169–171 dec	+47.1			
N-Acetyl (9)	133–135	−6			
3-Amino-3-deoxy-L-ribose hydrochloride (10)	165 dec	+18.9	165 dec, 169 dec	+23, +18.6, +21	*c, d*
			[159–160 dec, 161 dec]	[−23, −23]	*c, e*
Methyl 3-amino-3-deoxy-β-L-arabinofuranoside (11)	Syrup		[Syrup]		*f*
N-Isopropylidene (12)	162–163	+95.8	[155–157]	[−96]	*f*
N-Acetyl (13)	160–161	+125	[155]	[−119]	*f*
3-Amino-3-deoxy-L-arabinose hydrochloride (14)	159–160 dec	+110	*ca.* 150 dec	+110	*g*
			[*ca.* 150, 159, 160 dec]	[−113, −112, −110]	*f, g*

[a] Brackets denote enantiomer. [b] See ref 6d. [c] See ref 2. [d] See ref 6c. [e] See B. R. Baker, R. E. Schaub, and H. M. Kissman, *J. Amer. Chem. Soc.*, **77**, 5911 (1955). [f] See ref 6a. [g] See ref 18.

Hydrogenation of **6** in the presence of hydrochloric acid and subsequent deionization led to syrupy methyl 3-amino-3-deoxy-β-L-arabinofuranoside (**11**) which was characterized as a crystalline *N*-isopropylidene derivative (**12**) and as an *N*-acetyl derivative (**13**). Acid hydrolysis produced known 3-amino-3-deoxy-L-arabinose hydrochloride (**14**) which was also identified by comparison with an authentic sample.

Physical constants of the amino sugars are presented in Table I together with the literature data that are available.

It is hoped that the new synthesis of aminopentofuranosides, which proceeds from a hexopyranoside without direct involvement of the glycosidic center, will lend itself to useful applications. It is conceivable, for instance, that synthetic nucleosides containing a hexopyranosyl residue could now be transformed into ones that possess a 3-amino-3-deoxy-pentofuranosyl residue, while 3-amino-3-deoxyhexopyranosyl nucleosides have recently been synthesized[17] *via* the dialdehyde–nitromethane cyclization.

Experimental Section

All evaporations were done *in vacuo* at a bath temperature not exceeding 35°; as some of the compounds are quite sensitive, particular care in work-up operations is advisable. Melting points were taken in an electric aluminum block apparatus equipped with a calibrated thermometer. Infrared spectra were obtained from Nujol mulls on a Beckman IR-8 instrument. Optical rotations were determined at about 23° using a Perkin-Elmer automatic polarimeter, Model 141, with compound concentrations of 0.4–1.2% unless otherwise indicated. Thin layer chromatography was performed on silica gel G with ether–chloroform–methanol, (14:5:1), and paper chromatography was obtained using Whatman No. 1 paper with pyridine–ethyl acetate–water–acetic acid (5:5:3:1).

Methyl 2,3,4-Tri-*O*-acetyl-6-deoxy-6-nitro-α-D-glucopyranoside (1).—Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside[14b] (32 g), sodium nitrite (8 g), and phloroglucinol (5 g) were dissolved, by stirring at room temperature for about 15 min, in a mixture of dimethyl sulfoxide (160 ml) and *N*,*N*-dimethylformamide (40 ml). A flask equipped with a mercury seal stirrer was used, and analytical grade solvents were employed without special pretreatment. After the dissolution of the reactants, the mixture was placed in a water bath held at 15–18° for 72 hr while moderate stirring was maintained. The mixture was then poured into ice-cold water (1.8 l.) to give a crystalline precipitate which was stirred for 15 min, isolated, washed well with cold water, and dried in the air. The yield of crude **1**, mp 177–178°, was 24 g (92.5%). One recrystallization from 95% ethanol gave 20.5 g of product: mp 180–182°, $[\alpha]_D$ +145° (chloroform) (lit. mp 181–182°, $[\alpha]_D$ +143°,[12,13] and mp 179–180°, $[\alpha]_D$ +145°[8]).

Methyl 6-Deoxy-6-nitro-α-D-glucopyranoside (2).—A solution of the triacetate **1** (18 g) in methanol (160 ml) containing methyl *p*-toluenesulfonate (0.2 ml) was refluxed under exclusion of moisture for 4 days. The filtered solution was evaporated to give a faintly yellowish syrup that crystallized when cooled at 5° for a few hours (more rapidly upon seeding). The white mass was triturated carefully with about 20 ml of dry, ice-cold ether, filtered quickly with suction, and placed in a desiccator while still permeated with ether. After drying *in vacuo* at 25°, the somewhat hygroscopic product weighed 10 g (87%) and melted at 107–108°. An analytical sample was recrystallized by slow dissolution in ether at 25° and cooling of the solution to +5°: the melting point was unchanged, $[\alpha]_D$ +131.8° (*c* 1.9 in water).

Anal. Calcd for $C_7H_{13}NO_7$ (223.2): C, 37.67; H, 5.87; N, 6.28. Found: C, 37.55; H, 6.01; N, 6.11.

The methanolysis may be monitored by thin layer chromatography. It can be seen that **1** (R_f *ca.* 0.8) is converted into **2** (R_f *ca.* 0.1) with a temporary occurrence of several spots of intermediate speed, presumably partially deacetylated products.

The reaction time for the methanolysis can be shortened to 24 hr by increasing the amount of methyl *p*-toluenesulfonate tenfold, or by using anhydrous *p*-toluenesulfonic acid. However, such acceleration was accompanied by a decrease in yield and purity of **2**. The crude product tended to be discolored and to remain sticky on trituration with ether. A reasonable quantity of pure **2** could nevertheless be obtained by recrystallization from a larger amount (150–200 ml) of ether, with discarding of the insoluble, viscous contaminants.

Methyl 3-Deoxy-3-nitro-β-L-ribofuranoside (5).—Solutions of nitro glycoside **2** (3.35 g, 15 mmol) in 20 ml of 95% ethanol and of periodic acid (7.00 g, 99.5% H_5IO_6, slightly more than 30 mmol) in 50 ml of the same solvent were mixed in an ice bath, and the mixture was kept in the dark for 3 hr at +5° and overnight at 25°. Iodic acid that had crystallized out was removed and washed with a small amount of cold, absolute ethanol, and the combined filtrates were diluted with a twofold volume of water. The acidic solution was neutralized to pH 6 by cautious, dropwise addition, with efficient stirring, of 0.2 *N* barium hydroxide solution. The inorganic precipitate was filtered off and the filtrate was diluted with water to a volume of 400 ml. Now the solution was made slightly alkaline with 1 *N* potassium hydroxide so that the pH reached 7.5 and remained at that value for at least 15 min. The solution was allowed to stand for another 90 min at room temperature and was then deionized with Rexyn 101 (H^+).

It was observed by thin layer chromatography that slow-moving **2** had disappeared, after the periodic acid oxidation, to yield a fast moving spot (presumably the dialdehyde **3**), and that the later in turn had given way to two ill-separated spots of intermediate mobility (presumably mixture **4**) when the

(17) K. A. Watanabe and J. J. Fox, *J. Org. Chem.*, **31**, 211 (1966); F. W. Lichtenthaler and H. P. Albrecht, *Ber.*, **99**, 575 (1966); and other papers from the same laboratories.

reaction with alkali at pH 7.5 and subsequent deionization were finished.

To the pale yellow, deionized reaction solution was added sodium borohydride (2 g), and upon standing at 23° for 18 hr the solution was neutralized (but not rendered acidic) with dilute sulfuric acid. The mixture was extracted by shaking with four 150-ml portions of ethyl acetate, and the combined extracts, after drying over sodium sulfate, were concentrated at low temperature to about one-tenth their volume. An equal volume of ether was added and the mixture was cooled (0°) for 1 hr, whereby boric acid crystallized. The filtrate from the latter was diluted with an equal volume of ether and stored overnight at −5°, to deposit most of the remaining boric acid. To the filtrate therefrom was added petroleum ether (bp 30–60°) which caused the separation of an oil (A). The supernatant solution deposited crystals (B) on being stored overnight at +5°, and the mother liquor from B gave a syrup (C) upon evaporation.

The crystals B (560 mg, mp 100–105°) were crude **5**. Three recrystallizations from ethyl acetate–chloroform (1:4) gave pure **5**: mp 114–116°, $[\alpha]_D$ +32.5 (water). The material gave a single spot (R_f 0.45) on tlc and exhibited broad hydroxyl absorption in the 3300-cm^{-1} region and a nitro band at 1550 cm^{-1}.

Anal. Calcd for $C_6H_{11}NO_6$ (193.2): C, 37.31; H, 5.74; N, 7.25. Found: C, 37.19; H, 5.59; N, 7.15.

The oil A and syrup C gave nearly identical infrared spectra and thin layer chromatograms (two spots, R_f 0.45 and 0.50) and were therefore combined. The material was dissolved in a mixture of ethyl acetate and chloroform (1:1) from which additional **5** crystallized. The mother liquor was evaporated and the crystallization procedure was repeated with the residue; a total of 140 mg of impure **5** (mp >100°) was collected. Finally the remaining solution was evaporated to a syrup (D) that was rich in the compound with R_f 0.50.

Methyl 3-Deoxy-3-nitro-β-L-arabinofuranoside (6).—The syrup D was triturated with cold chloroform, which induced crystallization of a material melting at 70–80° and showing $[\alpha]_D$ +112° (water). It was **6** containing some of the isomer **5**. By fractional crystallization with ethyl acetate–chloroform the less soluble **5** could be removed, and eventually **6** was obtained as crystals (65 mg) that gave a single spot (R_f 0.50) on tlc: mp 68–71°, $[\alpha]_D$ +128° (water). The infrared spectrum showed a broad double peak (3470, 3350 cm^{-1}) for hydroxyl and a band at 1555 cm^{-1} for the nitro group.

Anal. Calcd for $C_6H_{11}NO_6$ (193.2): C, 37.31; H, 5.74; N, 7.25. Found: C, 37.39; H, 5.83; N, 7.45.

Methyl 3-Amino-3-deoxy-β-L-ribofuranoside Hydrochloride (7).—Compound **5** (300 mg) in water (90 ml) was hydrogenated at ordinary temperature and pressure in the presence of platinum catalyst (400 mg of PtO_2, prehydrogenated) and 1 *N* hydrochloric acid (1.7 ml). Hydrogen uptake (95 ml, *ca.* 90% of the theoretical) was rapid initially and ceased after 2 hr. The catalyst was removed and the solution, whose pH was adjusted to 5–6 by treatment with a small amount of Amberlite IR-45(OH^-), was evaporated to give a colorless syrup that crystallized easily after several evaporations with ethanol. The crystals were washed with cold absolute ethanol: yield 275 mg (88.5%), mp 165–166° dec, $[\alpha]_D$ +47.7° (water). Recrystallization from 95% ethanol–ether gave needles: mp 169–171° dec, $[\alpha]_D$ +46.1° (water). Paper chromatography showed a single spot, $R_{glucosamine}$ 2.8.

Anal. Calcd for $C_6H_{14}ClNO_4$ (199.6): C, 36.09; H, 7.07; N, 7.02. Found: C, 36.29; H, 7.29; N, 7.08.

Methyl 3-Amino-3-deoxy-β-L-ribofuranoside (8).—The hydrochloride **7** (60 mg) was converted into the free amine **8** by deionization using Dowex 1-X-2 (CO_3^{2-}). The aqueous solution was evaporated and the residue crystallized by trituration with absolute ethanol. Recrystallized from 95% ethanol–ether, **8** had mp 110–113° (111–113°, after a second recrystallization), $[\alpha]_D$ +32.7° (water).

Anal. Calcd for $C_6H_{13}NO_4$ (163.2): C, 44.16; H, 8.03; N, 8.58. Found: C, 44.20; H, 8.12; N, 8.54.

Methyl 3-Acetamido-3-deoxy-β-L-ribofuranoside (9).—The crude amine **8** obtained in another deionization of **7** (60 mg) was dissolved in methanol (2 ml) and treated with acetic anhydride (0.06 ml) at 25°. The mixture was evaporated after 15 min, leaving a residue which was evaporated once with toluene (10 ml) and twice with absolute ethanol. The colorless syrup obtained crystallized at −2° within 2 hr to give crude **9** (mp 125–126°) that was isolated by trituration with ethyl acetate. Recrystallization, effected from a large amount of ethyl acetate by evaporation in the air, gave diamond-shaped prisms: mp 133–135°, $[\alpha]_D$ −6° (water). Infrared maxima were at 3430 and 3280 (broad) and at 1635 and 1555 cm^{-1} (amide).

Anal. Calcd for $C_8H_{15}NO_5$ (205.2): C, 46.82; H, 7.37. Found: C, 46.95; H, 7.51.

3-Amino-3-deoxy-L-ribose Hydrochloride (10).—A solution of glycoside hydrochloride **7** (40 mg) in water (1 ml) and 1 *N* hydrochloric acid (4.5 ml) was heated on a steam bath for 17 hr. The hydrolysate was evaporated with several additions of water, at as low a temperature as practicable. A readily crystallizing syrup was obtained and the crystals, isolated by trituration with a little acetic acid, melted at 155–157° dec, $[\alpha]_D$ +22.4° (water). After two recrystallizations from water (0.2 ml)–acetic acid (1.5 ml) the product showed mp 158–160° dec, $[\alpha]_D$ +20.5°, and, after two further recrystallizations, mp 165° dec, $[\alpha]_D$ +18.9° (water). Identity with an authentic sample of **10**[2] was established by an undepressed mixture melting point and equal mobility in paper chromatography (see also Table I).

Methyl 3-Deoxy-3-isopropylidenamino-β-L-arabinofuranoside (12).—Compound **6** (140 mg) in water (50 ml) containing 1 *N* hydrochloric acid (0.9 ml) was hydrogenated (uptake, 55 ml of H_2 within 90 min) as described for **5**. A strongly dextrorotatory, ninhydrin-positive syrup was obtained which failed to crystallize. A paper chromatogram showed essentially one spot, $R_{glucosamine}$ 2.1; a faster moving trace spot suggested the starting material may have contained a small amount of the isomer **5**. The syrup was deionized as described for the hydrochloride **7**, but the free amine (**11**) likewise did not crystallize. It was therefore converted into its *N*-isopropylidene derivative **12** according to the directions given for the β-D enantiomer.[6a] The crystalline product (65 mg of mp 163–165° and $[\alpha]_D$ +93.4° in water, plus another 40 mg of lower, unsharp melting point from the mother liquor) was recrystallized twice from acetone and then showed mp 162–163°, $[\alpha]_D$ +95.8° (water), in accord with the literature values of the enantiomer (Table I). The infrared spectrum exhibited a hydroxyl band (3440 cm^{-1}) and C=N stretching vibrations (1690–1630 cm^{-1}).

Methyl 3-Acetamido-3-deoxy-β-L-arabinofuranoside (13).—A solution of the *N*-isopropylidene derivative **12** (30 mg) and acetic anhydride (0.04 ml) in methanol (2 ml) was kept at room temperature for 15 min and was then evaporated with additions of toluene (5 ml) followed by two 5-ml portions of ethanol. The white solid (**13**) was recrystallized from ethyl acetate, $[\alpha]_D$ +125° (water), mp 160–161° (unchanged after another recrystallization), in fair accord with data reported for the enantiomer (Table I). Infrared absorption was at 3400 and 3300 (broad double peak) and 1640 and 1545 cm^{-1} (amide bands). The spectra of **13** and the *ribo* isomer **9** were very similar over-all but showed distinct differences in band positions in the fingerprint region.

3-Amino-3-deoxy-L-arabinose Hydrochloride (14).—Syrupy glycoside hydrochloride obtained in a hydrogenation of **6** (120 mg) as described above was dissolved in water (20 ml) containing 1 *N* hydrochloric acid (0.65 ml). The hydrolysate was evaporated, the residue was treated with activated charcoal in water, and the colorless solution was evaporated to give a syrup that crystallized on trituration with a few drops of acetic acid and isopropyl alcohol. The crystals (mp 159° dec, with prior gradual darkening) were recrystallized from water (0.5 ml) by cautious addition of acetic acid to beginning turbidity followed by storage at +5° overnight: $[\alpha]_D$ +110° (water), mp 159–160° dec (gradual darkening from 145°, unchanged upon admixture with an authentic sample[18] of **14**). See also Table I. The product and an authentic sample had equal mobility in paper chromatography.

Registry No.—**1**, 4969-34-0; **2**, 16667-92-8; **5**, 17393-07-6; **6**, 17393-08-7; **7**, 17519-21-0; **8**, 17393-10-1; **9**, 17393-11-2; **10**, 17414-42-5; **11**, 17414-43-6; **12**, 17393-12-3; **13**, 17393-13-4; **14**, 17393-14-5.

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(18) H. H. Baer and A. Ahammad, *Can. J. Chem.*, **41**, 2931 (1963).