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Nitromethane-Condensation Reaction with 5-Aldehydes of Pentodialdofuranosides

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Treatment of methyl 2,3-di-O-benzyl-α-L-*arabino*-pentodialdo-1,4-furanoside (**1**) with nitromethane in the presence of sodium methoxide afforded an epimeric mixture of methyl 2,3-di-O-benzyl-6-deoxy-6-nitro-α-L-altro- (**2c**) and -β-D-galactofuranoside (**3c**) in a ratio of 2.5:1. On the other hand, the analogous treatment of 3-O-benzyl-1,2-O-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**7b**) with nitromethane gave 3-O-benzyl-6-deoxy-1,2-O-isopropylidene-6-nitro-α-D-glucofuranose (**8b**) predominantly.

In our previous papers,[2] syntheses of methyl 2,3-di-O-benzyl-α-L-*arabino*-pentodialdo-1,4-furanoside (**1**) and its β-anomer from D-glucose, D-galactose, or L-arabinose were reported. In connection with other synthetic studies on aminosugars, we investigated the condensation reaction of nitromethane with the aldehyde group of these compounds which forms the subject of this paper.

Following the method of Grosheintz and Fischer,[3] treatment of **1** with nitromethane in the presence of sodium methoxide afforded the desired mixture of methyl 2,3-di-O-benzyl-6-deoxy-6-nitro-α-L-altro- (**2a**) and-β-D-galactofuranoside (**3a**) in a good yield. However, each component of the syrupy mixture could not be detected separately on thin-layer chromatography, and the attempted formation of acetyl, benzyl, or tetrahydropyranyl derivative did not afford any crystalline substance suitable for isolation. Accordingly, characterization of **2a** and **3a** was carried out by the two following ways.

Without any purification, the mixture of **2a** and **3a** was reduced with lithium aluminum hydride in ether and gave a mixture of methyl 6-amino-2,3-di-O-benzyl-6-deoxy-hexofuranosides[4] (**2b** and **3b**) which was treated with acetic anhydride in methanol. The resulting mixture of the N-acetyl derivatives (**2c** and **3c**) was chromatographed on a silica gel column and afforded methyl 6-acetamido-2,3-di-O-benzyl-6-deoxy-α-L-altro- (**2c**) as a syrup and -β-D-galactofuranoside (**3c**) as crystals of mp 93—94°. These products were identified, respectively, with the samples synthesized by an unequivocal method in the following way: Monobenzoylation of methyl 2,3-di-O-benzyl-β-D-galactofuranoside[2c] (**3d**), followed by tosylation, gave methyl 6-O-benzoyl-2,3-di-O-benzyl-5-O-tosyl-β-D-galactofuranoside, which was treated with sodium methoxide to afford methyl 5,6-anhydro-2,3-di-O-benzyl-α-L-altrofuranoside (**4**). Ammonolysis of **4**, followed by N-acetylation of the resulting 6-amino-6-deoxy-furanoside (**2b**), yielded **2c** as a colorless liquid, which was identified with the sample obtained as above by its thin-layer chromatography and infrared spectrometry. On the

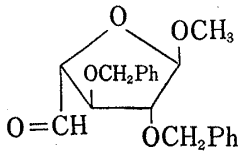
1) Location: *Hiromachi, Shinagawa-ku, Tokyo.*

2) *a*) T. Iwashige and H. Saeki, *Chem. Pharm. Bull.* (Tokyo), **15**, 132 (1967); *b*) H. Saeki, T. Iwashige and E. Ohki, *Chem. Pharm. Bull.* (Tokyo), **16**, 1040 (1968); *c*) H. Saeki and T. Iwashige, *Chem. Pharm. Bull.* (Tokyo), **16**, 962, (1968).

3) J.M. Grosheintz and H.O.L. Fischer, *J. Am. Chem. Soc.*, **70**, 1576 (1948).

4) The 6-amino-6-deoxy mixture was accompanied with by-products free from nitrogen, which probably originated from retrogression of the nitromethane-condensation products during the reduction.

other hand, treatment of methyl 2,3-di-O-benzyl-6-O-tosyl-β-D-galactofuranoside[5] (**3e**) with sodium azide in dimethyl sulfoxide, followed by reduction of the resulting 6-azido-6-deoxyfuranoside (**3f**) with lithium aluminum hydride, yielded a 6-amino-6-deoxy compound (**3b**). The N-acetylation of **3b** gave **3c** which was also idntified with the sample described above by thin-layer chromatography, mixed melting point test and infrared spectrometry.



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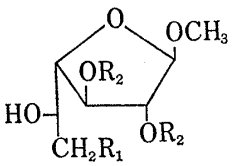
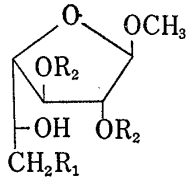
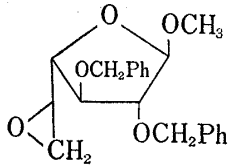


2a : $R_1=NO_2$, $R_2=CH_2Ph$
b : $R_1=NH_2$, $R_2=CH_2Ph$
c : $R_1=NHAc$, $R_2=CH_2Ph$
d : $R_1=NH_2$, $R_2=H$



3a : $R_1=NO_2$, $R_2=CH_2Ph$
b : $R_1=NH_2$, $R_2=CH_2Ph$
c : $R_1=NHAc$, $R_2=CH_2Ph$
d : $R_1=OH$, $R_2=CH_2Ph$
e : $R_1=OTs$, $R_2=CH_2Ph$
f : $R_1=N_3$, $R_2=CH_2Ph$
g : $R_1=NH_2$, $R_2=H$



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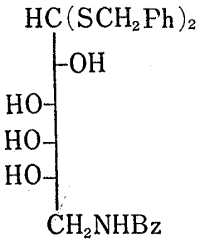

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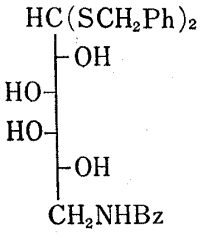

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For other structural proofs for the nitromethane-condensation products (**2a** and **3a**), an exhaustive hydrogenation of the epimeric mixture of **2a** and **3a** over palladium-charcoal at 70—80° afforded a mixture of methyl 6-amino-6-deoxy-α-L-altro- (**2d**) and -β-D-galactofuranoside (**3g**). Hydrolysis of the mixture of **2d** and **3g** with hydrochloric acid, followed by N-benzoylation of the resulting 6-amino carbohydrates and successive treatment with benzylthiol in the presence of an acid, gave a mixture of 6-benzamido-6-deoxyhexose dibenzyldithioacetals (**5** and **6**). Column chromatography of the dithioacetal mixture on silica gel, followed by repeated recrystallizations, yielded 6-benzamido-6-deoxy-L-altrose dibenzyl dithioacetal (**5**) as silky needles, mp 156—156.5°, and 6-benzamido-6-deoxy-D-galactose dibenzyl dithioacetal (**6**) as needles, mp 153—155°. By mixed melting point test and infrared spectrometry, these dithioacetals (**5** and **6**) were identified with the samples derived from the corresponding authentic samples by an analogous treatment.

The relative ratio of the reaction products, 6-deoxy-6-nitro-α-L-altro- (**2a**) and -β-D-galactofuranoside (**3a**), was determined as 2.5:1 in the following way. The debenzylated, fully hydrogenated mixture (**2d** and **3g**) obtained as described above was, without any purification, N-acetylated and then fully trimethylsilylated in an usual way. The resulting mixture was gas chromatographed at 187° on a column packed with 1.5% SE-30 silicone gum on Chromosorb W, during which authentic samples were utilized for comparison.

In 1963, Paulsen[6] reported that condensation reaction of 1,2-O-cyclohexylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**7a**) with nitromethane gave a mixture of 1,2-O-cyclohexyl-

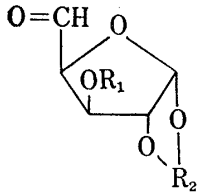
5) **3e** was obtained by tosylation of **3d** as a minor product as described in the experimental section. See also H. Saeki, T. Iwashige, and E. Ohki, *Chem. Pharm. Bull.* (Tokyo), **16**, 188 (1968).

6) H. Paulsen, *Ann. Chem.*, **665**, 166 (1963). It was also reported that condensation of 1,2-O-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose[3] or ethyl 2-acetamido-2-deoxy-α-D-*xylo*-pentodialdo-1,4-thiofuranoside[7] with nitromethane yielded a mixture of analogous 6-deoxy-6-nitrofuranosides, whose relative ratio, however, was not given.

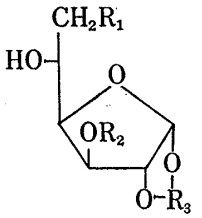
7) M.L. Wolfrom, S.M. Olin, and W.J. Polyglase, *J. Am. Chem. Soc.*, **72**, 1724 (1950).

idene-6-deoxy-6-nitro-α-D-gluco- (**8a**) and-β-L-idofuranose (**9a**) in a ratio of *ca.* 3:1. When Paulsen's result is compared with ours, there is a similarity of interest between these relative ratios of reaction products. When attention is focussed on the location of substituents at the C–4 and C–5 positions, Newman formula of the four nitro compounds could be depicted in their most stable conformations as illustrated in Chart 2 (**10**—**13**). Presuming that the size of the substituents falls in the order of nitromethyl>hydroxyl>hydrogen (for C–5), and C–3 hydroxylmethine> ring oxygen>hydrogen (for C–4), it was deduced, from the consideration of gauche interactions[8] between these groups, that D-gluco (**10**) or L-altro (**12**) form is more thermodynamically stable than L-ido (**11**) or D-galacto (**13**) form. Based on such a fact, predominant formation of D-gluco- (**10**) and L-altro–furanoside (**12**) in the nitromethane–condensation reaction will be explained by their greater structural thermostability, which forces the equilibrium of products (**10**⇄**11** or **12**⇄**13**) far in favor of **10** or **12**.

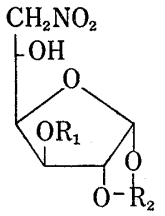
Expecting a more marked effect of the relative size of the substituents to the reaction mode, we next attempted the analogous nitromethane–condensation of 3-O-benzyl-1,2-O-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose[9] (**7b**), having a bulky group at the 3-position.



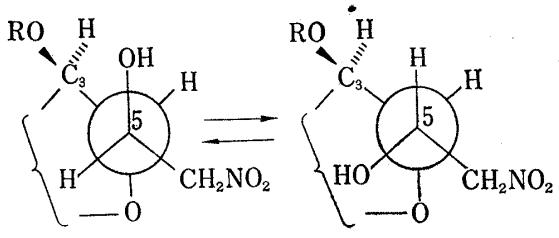
7a : R_1=H, R_2=cyclohexylidene
b : R_1=CH_2Ph, R_2=isopropylidene



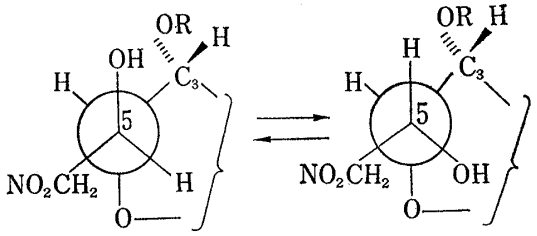
8a : R_1=NO_2, R_2=H, R_3=cyclohexylidene
b : R_1=NO_2, R_2=CH_2Ph, R_3=isopropylidene
c : R_1=NH_2, R_2=H, R_3=isopropylidene



9a : R_1=H, R_2=cyclohexylidene
b : R_1=CH_2Ph, R_2=isopropylidene



10 D-gluco- **11** L-ido-



12 L-altro- **13** D-galacto-

Treatment of **7b** with nitromethane was also carried out in the presence of sodium methoxide and the manner of its reaction was pursued by thin-layer chromatography. In about 10 minutes after the start of the reaction, all of **7b** was already converted into two products which might be 6-deoxy-6-nitro-gluco- (**8b**) and -ido-furanoside (**9b**). It was further observed that, by longer standing, one compound was gradually transformed into the other. After 1 hour or so, the latter product was the only one predominantly detected. The reaction products thus obtained could not be characterized, but the main component isolated by chromatography on a silica gel column, was hydrogenated over palladium charcoal to give 6-amino-6-deoxy-1,2-O-isopropylidene-α-D-glucofuranose (**8c**) in 70% yield from **7b**. The hydrochloride of **8c**, mp 192—194° (decomp.), was identified with the authentic sample.[10]

8) E.L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co. Inc., N.Y., 1962, p. 138.
9) M.L. Wolfrom and S. Hanessian, *J. Org. Chem.*, **27**, 1800 (1962).
10) R.L. Whistler and M.L. Wolfrom (ed.), "Methods in Carbohydrate Chemistry," Vol. I, Academic Press, N.Y. and London, 1962, p. 242.

This fact suggests that the bulky 3-O-benzyl group has a greater effect on the equilibrium between **8b** and **9b**, predominantly in the direction of the formation of **8b**. In spite of many efforts, an attempted detection of the possible isomer, 3-O-benzyl-6-deoxy-1,2-O-isopropylidene-6-nitro-β-L-idofuranose (**9b**), is not yet successful at present due to the scarcity and complexity of the by-products.

Experimental

Melting points are not corrected. Infrared spectra were determined on Perkin-Elmer Model 21. Analyses by gas-liquid chromatography were conducted with a Shimadzu Model GC-1B programmed vapor-phase chromatograph. Plates for thin-layer chromatography were prepared with Silica-Gel G (E. Merck AG). Visualisation of spots was effected by spraying conc. H_2SO_4, followed by heating.

Nitromethane-condensation of Methyl 2,3-Di-O-benzyl-α-L-*arabino*-pentodialdo-1,4-furanoside (1)—A mixture of 1.09 g of **1**, 0.98 g of $MeNO_2$, and 6 ml of abs. MeOH was adjusted to pH 9—10 with 1N $NaOCH_3$ methanolic solution and the mixture was stirred for 1 hr at room temperature. The reaction product was neutralized with AcOH with cooling and concentrated *in vacuo*. The residue were dissolved in 25 ml of $CHCl_3$ and washed three times with 10 ml of H_2O. The combined washings were extracted with $CHCl_3$ and the $CHCl_3$ solution was dried over anhyd. Na_2SO_4. Evaporation of the solvent *in vacuo* afforded 1.3 g of a syrup which was chromatographed on a silica gel column (40 g). Evaporation of the solvent from the fractions eluted with 20% (v/v) AcOEt-hexane gave an epimeric mixture of 6-deoxy-6-nitrofuranosides (**2a** and **3a**) as a colorless syrup which revealed only one spot on thin-layer chromatogram. The infrared spectrum of this mixture indicated the presence of a nitro group at 1550 cm^{-1} without any carbonyl absorption. *Anal.* Calcd. for $C_{21}H_{25}O_7N$: C, 62.52; H, 6.25; N, 3.42. Found: C, 62.77; H. 6.32; N, 3.31.

The 6-nitrofuranoside mixture (0.67 g) (**2a** and **3a**) was dissolved in 15 ml of dry ether and 0.2 g of $LiAlH_4$ was added with cooling and stirring. After stirring the mixture for 1 hr at room temperature, excess of the reagent was decomposed by dropwise addition of H_2O. This mixture was filtered, the filtrate was washed with H_2O, dried over anhyd. Na_2SO_4, and evaporated *in vacuo* to give 0.46 g of a syrup (**2b** and **3b**) which was dissolved in 5 ml of methanol and 1 ml of Ac_2O was added. The mixture was kept for 1 hr at room temperature, the solvent was evaporated *in vacuo* to dryness, and left 0.50 g of an N-acetate mixture (**2c** and **3c**). The N-acetate mixture (**2c** and **3c**) was charged on a silica gel column (15 g) and eluted with hexane containing increasing gradient of 30—70% (v/v) of AcOEt. Thus, accompanied with 185 mg of by-products not containing nitrogen function, 185 mg of methyl 6-acetamido-2,3-O-benzyl-6-deoxy-α-L-altrofuranoside (**2c**), a colorless syrup, and 48 mg of methyl 6-acetamido-2,3-O-benzyl-6-deoxy-β-D-galactofuranoside (**3c**), needles, mp 93—94°, were obtained. These products were identified by thin-layer chromatography, and infrared spectrometry with the authentic samples.

A mixture of the 6-deoxy-6-nitrofuranosides (**2a** and **3a**) (1.23 g) was hydrogenated over 0.75 g of 10% Pd-C at 27 kg/cm^2 and 70—80° in 30 ml of EtOH and 15 ml of AcOH. After filtration of the catalyst, the reaction mixture was evaporated to dryness *in vacuo* and the resulting debenzylated product (**2d** and **3g**) was hydrolysed in 50 ml of 2 N HCl by heating on a steam bath for 4 hr. After treatment with Norit or Darco G-60, the reaction mixture was evaporated to dryness *in vacuo* and left 0.65 g of a syrup. This syrupy mixture of the amino-carbohydrates was dissolved in 5 ml of H_2O containing 0.9 g of $KHCO_3$, and 0.5 ml of BzCl was added with cooling and stirring. The mixture was allowed to stand overnight, diluted with H_2O, and passed through 15 ml of Amberlite IR-120 (H^+), neutralized with Amberlite IR-45 (OH^-), and evaporated to dryness below 50° *in vacuo*. Extraction of the residue with EtOH and evaporation of the solvent afforded 350 mg of N-benzoates as a powder, which was treated with benzylthiol in the presence of an acid in the usual manner. The crystalline dibenzyl dithioacetals were separated by repeated recrystallization from EtOH and a column chromatography on silica gel with 3% (v/v) MeOH-$CHCl_3$. The product gave 228 mg of 6-benzamido-6-deoxy-L-altrose dibenzyl dithioacetal (**5**) as silky needles, mp 156—156.5°, and 65 mg of 6-benzamido-6-deoxy-D-galactose dibenzyl dithioacetal (**6**) as needles, mp 153—155°. *Anal.* Calcd. for $C_{27}H_{31}O_5NS_2$: C, 63.14; H, 6.08; N, 2.73; S, 12.49. Found (for **5**): C, 63.15; H, 6.10; N, 2.61; S, 12.52. Found (for **6**): C, 62.65; H, 5.96; N, 2.59; S, 12.25.

The relative ratio of the $MeNO_2$-condensation products (**2a** and **3a**) was determined in the following way: The foregoing reaction product (167 mg) dissolved in a mixture of 15 ml of EtOH and 1 ml of AcOH was hydrogenated over 0.1 g of 10% Pd-C at 38 kg/cm^2 and at 70—80°. After filtration of the catalyst, the mixture was evaporated to dryness *in vacuo*, and the residue was dissolved in a few ml of MeOH. After addition of 0.2 ml of Ac_2O with stirring, the mixture was kept for 1 hr at room temperature and evaporated *in vacuo* to dryness. The residue was fully trimethylsilylated in the usual manner for gas-liquid chromatography. The authentic samples for comparison were also prepared in the same way. The relative ratio of **2a** and **3a** was determined as 2.5:1 by gas-liquid chromatography of these N-acetyl-trimethylsililated samples.

Methyl 6-O-Benzoyl-2,3-di-O-benzyl-β-D-galactofuranoside——To an ice-cold solution of 11.22 g of methyl 2,3-di-O-benzyl-β-D-galactofuranoside[2c] (**3d**) in 50 ml of pyridine, 3.88 ml of BzCl was added dropwise with stirring, the mixture was stirred for 15 min at 0°, and then for 4 hr at room temperature. The mixture was poured into ice-water and extracted twice with $CHCl_3$. The extract was washed successively with dil.HCl, H_2O, dil. NaOH, and H_2O and dried over anhyd.Na_2SO_4. Evaporation of the solvent gave 13.6 g of a pale yellow syrup which revealed 2 spots on thin-layer chromatogram. The crude benzoate mixture was chromatographed over 150 g of silica gel, and evaporation of the solvent from fractions eluted with 5% (v/v) AcOEt-benzene afforded 1.76 g of methyl 5,6-di-O-benzoyl-2,3-di-O-benzyl-β-D-galactofuranoside as a fast-moving component and 7.58 g of a chromatographically pure 6-monobenzoate as a colorless syrup. The infrared spectrum of the 6-monobenzoate indicated the presence of a hydroxyl group. Analytically pure sample of the monobenzoate was not obtained. *Anal.* Calcd. for $C_{28}H_{30}O_7$: C, 70.28; H, 6.32. Found: C, 69.32; H, 6.16.

Methyl 6-O-Benzoyl-2,3-di-O-benzyl-5-O-tosyl-β-D-galactofuranoside——To a solution of 6.15 g of methyl 6-O-benzoyl-2,3-di-O-benzyl-β-D-galactofuranoside in 30 ml of pyridine was added 5 g of TsCl, and the mixture was allowed to stand for 3 days at room temperature. Then the mixture was poured into ice-water and extracted with ether. The extract was washed successively with dil.HCl, dil.$NaHCO_3$, and H_2O, and dried over anhyd. Na_2SO_4. Removal of the solvent *in vacuo* gave 8.15 g of methyl 6-O-benzoyl-2,3-di-O-benzyl-5-O-tosyl-β-D-galactofuranoside as a pale yellow syrup. The analytical sample of $[\alpha]_D^{21}$ −7.2° (c=4.4, $CHCl_3$) was prepared by chromatography on a silica gel column. *Anal.* Calcd. for $C_{35}H_{36}O_9S$: C, 66.44; H, 5.73; S, 5.07. Found: C, 66.16; H, 5.73; S, 4.95.

Methyl 5,6-Anhydro-2,3-di-O-benzyl-α-L-altrofuranoside (**4**)——To a solution of 7.08 g of methyl 6-O-benzyl-2,3-di-O-benzyl-5-O-tosyl-β-D-galactofuranoside in 30 ml of $CHCl_3$ was added dropwise 15 ml of 1N NaOMe solution with cooling and stirring. The resulting mixture was allowed to stand for 4 days in a refrigerator. After decomposition of NaOMe by addition of solid CO_2, the mixture was diluted with 100 ml of $CHCl_3$, and washed with a saturated NaCl solution. The aqueous layer was washed with 50 ml of $CHCl_3$ and the combined $CHCl_3$ solution and washings were dried over anhyd.Na_2SO_4. Evaporation of the solvent *in vacuo* at 100—120° (bath temp.) gave 3.4 g of a syrup which revealed one spot on thin-layer chromatogram. The syrup was chromatographed on 50 g of silica gel and eluted with benzene. Removal of the solvent yielded 2.96 g of **4**, colorless syrup, $[\alpha]_D^{23}$ −50.3° (c=9.8, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{24}O_5$: C, 70.76; H, 6.79. Found: C, 70.44; H, 6.88.

Methyl 6-Acetamido-2,3-di-O-benzyl-6-deoxy-α-L-altrofuranoside (**2c**)——A mixture of a solution of 0.54 g of **4** in 10 ml of MeOH and 50 ml of NH_3-saturated MeOH was heated at 90—100° for 7 hr in a sealed tube. The crude amino-alcohol obtained by complete removal of the solvent was dissolved in 5 ml of MeOH, 1 ml of Ac_2O was added, and, the mixture was evaporated to dryness *in vacuo* after standing for 1 hr. The residue was chromatographed on a silica gel column and removal of the solvent from fractions eluted with 30—70% (v/v) AcOEt-hexane yielded 519 mg of **2c** as a colorless liquid. *Anal.* Calcd. for $C_{23}H_{29}O_6N$: C, 66.49; H, 7.04; N, 3.37. Found: C, 65.90; H, 6.98; N, 3.19.

Methyl 2,3-Di-O-benzyl-6-O-tosyl-β-D-galactofuranoside (**3e**) **and Methyl 2,3-Di-O-benzyl-5,6-di-O-tosyl-β-D-galactofuranoside**——To an ice-cold solution of 5.1 g of methyl 2,3-di-O-benzyl-β-D-galactofuranoside[2c] (**3d**) in 20 ml of pyridine was added 5.2 g of TsCl and the mixture was allowed to stand overnight at room temperature. The mixture was poured into ice-water and extracted with $CHCl_3$. The extract was washed successively with dil.HCl, H_2O, dil.NaOH solution, and H_2O, and dried over anhyd. Na_2SO_4. Evaporation of the solvent *in vacuo* gave a syrup which was chromatographed on a silica gel column. The fractions eluted with benzene gave 7.0 g (75%) of methyl 2,3-di-O-benzyl-5,6-di-O-tosyl-β-D-galactofuranoside, a colorless syrup, $[\alpha]_D^{21}$ −31.5° (c=3.6, $CHCl_3$). *Anal.* Calcd. for $C_{35}H_{38}O_{10}S_2$: C, 61.57; H, 5.61; S, 9.39. Found: C, 61.44; H, 5.78; S, 9.19.

The fractions eluted with 5% (v/v) ether-benzene yielded 0.9 g (12.5%) of **3e**, a colorless syrup, $[\alpha]_D^{19}$ −48.0° (c=4.6, $CHCl_3$). *Anal.* Calcd. for $C_{28}H_{32}O_8S$: C, 63.62; H, 6.10; S, 6.07. Found: C, 63.37; H, 6.15; S, 5.86.

Methyl 6-Azido-2,3-di-O-benzyl-6-deoxy-β-D-galactofuranoside (**3f**)——A mixture of 3.2 g of **3e**, 0.44 g of NaN_3, and 20 ml of dimethyl sulfoxide was heated on an oil bath at 90—100° for 2 hr with stirring in N_2 atmosphere. The cooled mixture was diluted with $CHCl_3$ and washed with H_2O. The $CHCl_3$ layer was dried over anhyd.Na_2SO_4 and evaporated *in vacuo*, giving 2.56 g of **3f** as a syrup which revealed one spot on thin-layer chromatogram. Its infrared spectrum did not indicate the presence of tosyl group, but of azide group. The analytical sample was prepared by chromatography on a silica gel column, $[\alpha]_D^{21}$ −77.8° (c=6.1, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{25}O_5N_3$: C, 63.14; H, 6.31; N, 10.52. Found: C, 62.91; H, 6.34; N, 10.27.

Methyl 6-Acetamido-2,3-di-O-benzyl-6-deoxy-β-D-galactofuranoside (**3c**)——To a solution of 0.58 g of **3f** in 10 ml of dry ether, 0.1 g of $LiAlH_4$ was added in small portions with cooling and the mixture was stirred for 2 hr at room temperature. The syrupy product thus obtained by treatment in the usual manner was dissolved in 6 ml of MeOH and 0.5 ml of Ac_2O was added. After standing for 2 hr at room temperature, the mixture was evaporated to dryness *in vacuo* and 0.36 g of residual crystals was recrystallized from iso-PrOH-hexane to give **3b** of mp 93—94°, $[\alpha]_D^{20}$ −30.7° (c=3.1, $CHCl_3$). *Anal.* Calcd. for $C_{23}H_{29}O_6N$: C, 66.49; H, 7.04; N, 3.37. Found: C, 66.64; H, 7.07; N, 3.67.

Nitromethane-condensation of 3-O-Benzyl-1,2-O-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (7b)—A solution of 1.26 g of **7b** and 1.6 ml of $MeNO_2$ in 30 ml of MeOH was adjusted to pH 8—9 by adding dropwise 1N NaOMe solution with cooling. The mixture was allowed to stand for 1.5 hr at room temperature and neutralized with AcOH with cooling. The resulting mixture was diluted with 80 ml of $CHCl_3$ and washed twice with a saturated NaCl solution. The organic layer was dried over anhyd. Na_2SO_4 and evaporated *in vacuo*, giving 1.64 g of a pale yellow syrup, which was chromatographed over 40 g of a silica gel column. Removal of the solvent from fractions eluted with 20% (v/v) AcOEt–hexane afforded 1.14 g (74%) of 6-deoxy-1,2-O-isopropylidene-6-nitro-α-D-glucofuranose (**8b**) as a colorless syrup which revealed one spot on thin-layer chromatogram. *Anal.* Calcd. for $C_{16}H_{21}O_7N$: C, 56.63; H, 6.24; N, 4.13. Found: C, 56.80; H, 6.30; N, 3.77. The above nitro-compound (**8b**) (1.07 g) was hydrogenated over 0.7 g of Pd–C in 40 ml of EtOH at 80 kg/cm² and 70°. After filtration of the catalyst, the mixture was evaporated to dryness *in vacuo*, giving 624 mg (90%) of 6-amino-6-deoxy-1,2-O-isopropylidene-α-D-glucofuranose (**8c**) which crystallized on digestion with ether. **8c** formed, quantitatively, a hydrochloride of mp 192—194° (decomp.) which was identical with the authentic sample synthesized by a known method[10] by mixed melting point test and infrared spectrometry.

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