Branched-chain Sugars. III. Addition of Vinylmagnesium Bromide to 5,6-Dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-3-*O*-substituted-*α*-D-*xylo*-hex-5-enofuranoses[1]

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Addition of vinylmagnesium bromide to 3-*O*-acetyl (**1**) and 3-*O*-benzyl (**3**) derivatives of 5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hex-5-enofuranose gave the corresponding 5-deoxy-5-*C*-vinyl derivatives of L-*ido*-type, of which the configurations were proved by intramolecular cyclization into the corresponding nitrocyclitols. Conformations of **1** and **3** and that of the transition state in the addition reaction were discussed on the basis of their NMR parameters.

In order to find out a synthetic passway of 5,6-dideoxy-5-*C*-formyl-6-*C*-nitro-D-glucose as a key intermediate for synthesis of tetrodotoxin from D-glucose,[2] addition of vinylmagnesium bromide to 5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-3-*O*-substituted-α-D-*xylo*-hex-5-enofuranoses was examined and the configuration of products were determined to be of L-*ido*-type by intramolecular cyclization into the corresponding branched-chain nitrocyclitols.

Results and Discussion

A few papers on addition of the Grignard reagents to nitroolefins have been published,[3-6] however, no report on the similar reaction of sugar derivatives has been appeared in literatures. Baer and Rank synthesized 3-*O*-acetyl-6-deoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hex-5-enofuranose (**1**) from 1,2-*O*-isopropylidene-α-D-glucofuranose by periodate oxidation, nitromethane condensation, 3,5-di-*O*-acetylation and elimination.[7] By the similar way, the corresponding 3-*O*-benzyl derivative (**3**) was obtained from 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose,[8] in which 5-*O*-acetyl-3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-idofuranose (**2**) was obtained as crystals. The configuration of **2** was determined by comparison of its optical rotation ($[\alpha]_D$ −58.2°) with that of the corresponding 3-*O*-acetyl derivatives (D-*gluco* type, $[\alpha]_D$ +18.8°; L-*ido* type, $[\alpha]_D$ −30.1°).[9]

Reaction of **1** and **3** with four equivalents of vinylmagnesium bromide in tetrahydrofuran at 0 °C gave 3-*O*-acetyl (**4**) and 3-*O*-benzyl (**5**) derivatives of 5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-5-*C*-vinyl-β-L-idofuranose in 28 and 41% yield, respectively. The epimeric D-*gluco*-type isomer could not be detected by NMR spectra. Reaction of **1** with other Grignard reagents such as methyl, allyl, β-styryl, and phenylmagnesium bromide gave only intractable sirups, and the original nitro group could not be detected in IR spectra of the products, when large excess amount of reagents were used. Vinyllithium reaction of **3** gave **5** in much lower yield than that of the Grignard reaction. Hydrogenation of **5** in the presence of palladium-charcoal gave quantitatively the corresponding 5-*C*-ethyl derivative (**6**).

In order to prove the configuration at *C*-5, both **4** and **5** were respectively de-*O*-isopropylidenated in 70% acetic acid at 80—85 °C for 7—8 hr under monitoring with tlc, and then the hydrolyzed products were intramolecularly cyclized into the corresponding nitro cyclitols, without separation in a pure state. In the case of **5**, cyclization in ethanol at pH 8—9 for 2 days and successive acid-catalyzed acetylation gave 2,4-di-*O*-acetyl-3-*O*-benzyl-1-*O*-ethyl-(1,3,5/2,4,6)-6-nitro-5-vinylcyclohexanetetrol (**7**)[10] in 83% yield. When the cyclization was performed in methanol–water in the presence of equimolar amount of sodium bicarbonate, 3-*O*-benzyl-(3,5/1,2,4,6)-6-nitro-5-vinylcyclohexanetetrol (**8**)[10] was obtained in 52% yield, which was then converted into the corresponding 1,2,4-tri-*O*-acetate (**9**). Acetylation of the sirup obtained from the mother liquor of **8** gave the *C*-1 epimer of **9** (**10**). The ratio of **10** to **9** was 1: 1.54. In the case of **4**, a similar cyclization and *O*-acetylation gave 1,2,3,4-tetra-*O*-acetyl-(1,3,5/2,4,6)-6-nitro-5-vinylcyclohexanetetrol (**11**)[10] as crystals in 11.4% yield. Hydrogenation of **8** in ethanol–acetic acid in the presence of platinum-charcoal gave 3-*O*-benzyl-(3,5/1,2,4,6)-6-amino-5-ethylcyclohexanetetrol (**12**)[10] as an acetate.

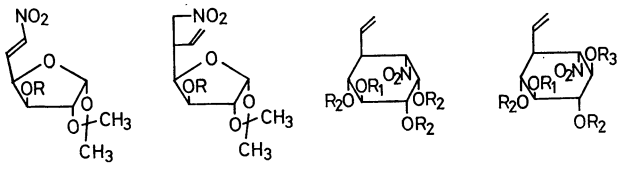
First-order analysis of NMR spectra of nitrocyclitols (**7**—**11**) by double resonance technique clarified their configurations (Table 1). The hydrogen signals at the branched point were distinguished by its multi-splittings and higher resonating magnetic field than others. Other ring-protons appeared in a lower field in the order of alkoxy, nitro, and acetoxy position. They have com-

1) Part II. This Bulletin, **46**, 1515 (1973).
2) J. Yoshimura, K. Kobayashi, K. Sato, and M. Funabashi, *ibid.*, **45**, 1806 (1972).
3) E. P. Kohler and J. F. Stone, *J. Amer. Chem. Soc.*, **52**, 761 (1930).
4) G. D. Buckley and E. Ellery, *J. Chem. Soc.*, **1947**, 1497.
5) A. Lambert, J. D. Rose, and B. C. L. Weedon, *ibid.*, **1949**, 42.
6) J. Colonge and G. Lartigan, *Bull. Soc. Chim. Fr.*, **1965**, 738.
7) H. H. Baer and W. Rank, *Can. J. Chem.*, **43**, 3330 (1965).
8) M. L. Wolfrom and S. Hanessian, *J. Org. Chem.*, **27**, 1800 (1962).
9) J. M. Grosheints and H. O. L. Fischer, *J. Amer. Chem. Soc.*, **70**, 1476 (1948).
10) For easier understanding, the numbering and figures of nitrocyclitols for nomenclature were cited from that of original compounds. Other points were followed by "Tentative Rules for Cyclitol Nomenclature" of IUPAC (1967 rule).

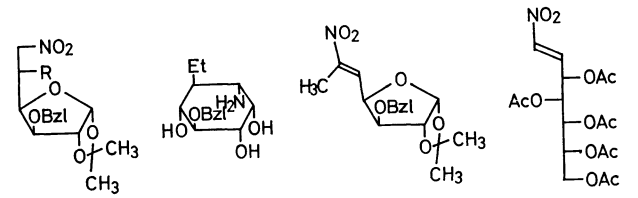
TABLE 1. NMR PARAMETERS OF *O*-ACETYLATED NITROCYCLITOLS

Compound	H_1	H_2	H_3	H_4	H_5	H_6	Other protons
7	3.95(t) $J_{1,2}=10.0$	5.27(t) $J_{2,3}=10.0$	3.64(t) $J_{3,4}=10.0$	5.04(t) $J_{4,5}=10.0$	2.72 $J_{5,6}=12.5$	4.47(dd) $J_{1,6}=10.0$	7.30 (Ph; m), 5.60 (H; m, $J_{5,7}=7.5$), 5.20—5.00 (H_{8a}, H_{8b}; m), 4.62 ($PhCH_2O$; s), 3.54 (OCH_2; q, $J_{CH_3,CH_2}=6.5$), 1.07 (CH_3; q), 2.00 and 1.93 (OAc; s).
9	5.95(t) $J_{1,2}=2.5$	5.00(dd) $J_{2,3}=10.0$	3.92(t) $J_{3,4}=10.0$	5.07(dd) $J_{4,5}=10.5$	3.25 $J_{5,6}=12.5$	4.65(dd) $J_{1,6}=2.5$	7.30 (Ph; m), 5.80—5.10 (H_7, H_{8a} and H_{8b}; m), 4.67 ($PhCH_2O$; s), 2.18, 2.00 and 1.98 (OAc).
10	5.60(t) $J_{1,2}=10.0$	5.20(t) $J_{2,3}=10.0$	3.75(t) $J_{3,4}=10.0$	5.08(dd) $J_{4,5}=12.5$	2.80 $J_{5,6}=12.5$	4.62(dd) $J_{1,6}=10.0$	7.29 (Ph; m), 5.60 (H_7; m), 5.2—5.0 (H_{8a}, H_{8b}; m), 4.62 ($PhCH_2O$; s), 2.08, 1.98 and 1.93 (OAc).
11	4.9—5.9 (H_1–H_4)			$J_{4,5}=10.5$	2.92 $J_{5,6}=10.5$	4.12 $J_{1,6}=12.5$	4.9—5.9 (H_7, H_{8a} and H_{8b}; $J_{5,7}=8.5$), 1.98 (4×OAc).

monly large *trans*-diaxial coupling constants except H_1 of **9**. Thus, the configuration of **4** and **5** was proved to be of L-*ido* type.



(**1**) R=Ac (**4**) R=Ac (**8**) R_1=Bzl, (**7**) R_1=Bzl,
(**3**) R=Bzl (**5**) R=Bzl R_2=H R_2=Ac,
(**9**) R_1=Bzl, R_3=Et
R_2=Ac (**10**) R_1=Bzl,
R_2=R_3=Ac
(**11**) R_1=R_2=
R_3=Ac



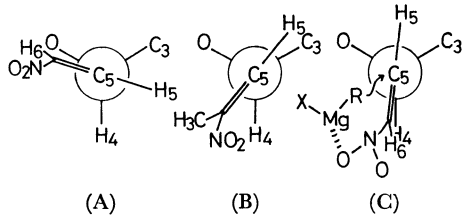
(**2**) R=OAc (**12**) (**13**) (**14**)
(**6**) R=Et

In order to deduce the conformation of nitroolefin function of **1** and **3**, 6-*C*-methyl derivative of **3** (**13**) was synthesized by a similar method to that of **3**, and also D-*gluco*-3,4,5,6,7-pentaacetoxy-1-nitro-1-heptene (**14**) from the corresponding 1-*C*-nitro-1-deoxyalditol[11] by the usual procedure.

NMR parameters of nitroolefin function of these compounds and 1-nitro-1-pentene (**15**)[12] (Table 2) showed that α-proton signals of **1** and **3** appear in the lower magnetic field than that of **14** and **15**, and $J_{\beta,\gamma}$ values in **1** and **3** are smaller than that of others. These facts indicate that the dihedral angle between H_4 and H_5 in **1** and **3** equals nearly 72°[13] in a conformation with a hydrogen-bonding between H_6 and the lactol oxygen, as shown in Fig. 1(A). While that of **13** means the angle should be larger than 140°, indicating the both protons are oriented to an almost true-*trans* as shown in (B).

TABLE 2. NMR PARAMETERS IN NITRO OLEFIN FUNCTIONS

Compound	(H_γ) (H_4)	(H_β) (H_5)	(H_α) (H_6)
1	5.05(t) $J_{4,5}=2.5$	7.10(dd) $J_{5,6}=13.0$	7.29(d)
3	4.91(t) $J_{4,5}=2.5$	7.13(dd) $J_{5,6}=15.5$	7.30(d)
13	4.82(dd) $J_{4,5}=7.5$	7.18(d)	
	(H_3)	(H_2)	(H_1)
14	5.62(m) $J_{2,3}=4.5$	7.22(dd) $J_{2,1}=14.0$	6.97(d)
15	2.30(q) $J_{2,3}=6.5$	7.30(td) $J_{2,1}=14.0$	7.06(d)



(A) (B) (C)

Fig. 1. Conformation of nitro olefin functions.

If conformation (A) is maintained in the transition state of the Grignard reaction, vinyl group will approach to C_5 from the less-hindered down-side to give D-*gluco* type product, however, the configuration of products were L-*ido* type. Therefore, it will be concluded that the conformation in the transition state

11) J. Yoshimura and H. Ando, *Nippon Kagaku Zasshi*, **85**, 138 (1964).
12) A. I. Meyers and J. C. Sircar, *J. Org. Chem.*, **32**, 4134 (1967).
13) E. W. Garbish, *J. Amer. Chem. Soc.*, **86**, 5561 (1964).

was changed from (A) to (B) by coordination of the Grignard reagent to the nitro-oxygen, and the vinyl group attacked from less-hindered lactol-oxygen site, as shown in (C).

Experimental

All melting points are uncorrected. The solutions were evaporated under diminished pressure at a bath temperature not exceeding 45 °C. Specific rotations were measured in a 0.5-dm tube, with a Carl Zeiss photoelectric polarimeter. The IR spectra were recorded with a Hitachi Model EPI-GS spectrophotometer. The NMR spectra were taken in deuteriochloroform with a JMN-4H-100 MHz Spectrometer using tetramethylsilane as an internal standard. Chemical shifts and coupling constants were recorded in δ and Hz units, and frequencies in cm^{-1}.

5-O-Acetyl-3-O-benzyl-6-deoxy-1,2-O-isopropylidene-6-C-nitro-β-L-idofuranose (2). To a solution of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (60 g, 0.193 mol)[8] in benzene (500 ml) was added lead tetraacetate (80 g, 0.20 mol) portionwise under refluxing, filtered after cooling, and evaporated. The residual sirup was extracted with chloroform, and the extract was washed with water, dried, and evaporated to give the corresponding 5-aldehyde derivative (56 g) as a sirup. A solution of the sirup and nitromethane (40 ml, 0.65 mol) in ethanol (100 ml) was adjusted to pH 7.8—8.0 with 2M-sodium hydroxide, stood at room temperature for 5 hr, neutralized with acetic acid, and evaporated. The residual sirup was extracted with chloroform, and the extract was washed twice with water, dried, and evaporated to give sirupy mixture of 6-deoxy-6-*C*-nitro derivatives (52 g). A solution of this sirup and *p*-toluenesulfonic acid (0.5 g) in acetic anhydride (50 ml) was kept at room temperature for 3.5 hr, poured into ice-water to give semi-crystalline product in 75.1% (55 g) total yield.

Recrystallization from ethanol gave a pure isomer in 47.2% (33.2 g) yield. Mp 96—97 °C, $[\alpha]_D^{33}$ −58.2° (*c* 0.97, chloroform); IR: 1740 (ester), 1550 and 1368 (NO_2); NMR: 7.36 (Ph; s), 5.92 (H_1; d, $J_{1,2}$=3.5), 5.73 (H_5; m), 4.92 and 4.68 (H_{6a} and H_{6b}; ABq, J_{ab}=14.0, $J_{5,6a}$=3.5, $J_{5,6b}$=7.5), 4.69 and 4.51 (-CH_2-; ABq, J_{ab}=11.5), 4.62 (H_2; d), 4.40 (H_4; dd, $J_{3,4}$=3.0, $J_{4,5}$=5.0), 4.07 (H_3; d), 2.03 (OAc), 1.51 and 1.36 (2×C-CH_3).

Found: C, 56.78; H, 5.98; N, 3.48%. Calcd for $C_{18}H_{23}NO_8$: C, 56.68; H, 6.08; N, 3.67%.

3-O-Benzyl-5,6-dideoxy-1,2-O-isopropylidene-6-C-nitro-α-D-xylo-hex-5-enofuranose (3). A solution of **2** (2.0 g, 5.25 mmol) in benzene (70 ml) was refluxed in the presence of potassium carbonate (4.0 g, 28.6 mmol), filtered, and evaporated to give a sirup (1.8 g). Fractionation of the sirup on a Kieselgel column with benzene as an effluent gave the pure product as a sirup (1.14 g, 71.3%). $[\alpha]_D^{23}$ −29.1° (*c* 0.96, chloroform); IR: 1650 (C=C), 1510 and 1340 (conjugated NO_2), 735 and 691 (Ph); NMR: 7.35 (Ph; m), 7.30 (H_6; d, $J_{5,6}$=15.5), 7.13 (H_5; dd, $J_{4,5}$=2.5), 6.01 (H_1; d, $J_{1,2}$=3.5), 4.91 (H_4; t, $J_{3,4}$=2.5), 4.68 (H_2; d), 4.68 and 4.46 (CH_2; ABq, $J_{a,b}$=11.5), 4.06 (H_3; d), 1.52 and 1.37 (2×C-CH_3).

Found: C, 60.07; H, 6.08; N, 4.58%. Calcd for $C_{16}H_{19}NO_6$: C, 59.80; H, 5.96; N, 4.36%.

3-O-Benzyl-5,6-dideoxy-1,2-O-isopropylidene-6-C-nitro-5-C-vinyl-β-L-idofuranose (5). To a solution of a sirupy **3** [3.5 g, obtained from 5 g (13.1 mmol) of **2**] in THF (30 ml) was added dropwise a solution of vinyl magnesium bromide[14] in THF (30 ml) prepared from magnesium (1.25 g, 52.4 mmol) and excess amount of vinyl bromide under ice-cooling. After stirring for 1 hr at room temperature, the reaction mixture was neutralized with acetic acid (6 ml) under cooling, and extracted with chloroform. Evaporation of the extract gave a sirup (3.5 g) which was crystallized from ethanol. Yield, 41% (1.86 g); mp 103 °C; $[\alpha]_D^{23}$ −71.4° (*c* 1.23, chloroform); IR: 1640 (C=C), 1540 and 1373 (NO_2). NMR: 7.34 (Ph; s), 5.88 (H_1; d, $J_{1,2}$=3.8), 5.65 (H_7; octet, $J_{5,7}$=8.5, $J_{7,8a}$=17.5, $J_{7,8b}$=10.0), 5.18 and 5.14 ($J_{8a,8b}$=2.5), 4.66 and 4.39 (CH_2; ABq, $J_{a,b}$=10.3), 4.58 (H_2; d), 4.39 (H_6; d, $J_{5,6}$=6.0), 4.14 (H_4; dd, $J_{4,5}$=6.8), 3.84 (H_3; d, $J_{3,4}$=3.0), 3.45 (H_5; m), 1.29 and 1.46 (2×C-CH_3).

Found: C, 62.08; H, 6.79; N, 3.98%. Calcd for $C_{18}H_{23}NO_6$: C, 61.88; H, 6.64; N, 4.01%.

3-O-Acetyl-5,6-dideoxy-1,2-O-isopropylidene-6-C-nitro-5-C-vinyl-β-L-idofuranose (4). In the same manner as **5**, **1** (2.68 g, 9.85 mmol) was treated with 4 equimolar amount of vinylmagnesium bromide in THF. Fractionation of the product on a Kiesel Gel 60 column gave 0.87 g (28%) of **4** as a sirup. $[\alpha]_D^{23}$ −35.6° (*c* 0.96, chloroform); IR: 1745 (ester), 1635 (C=C), 1544 and 1381 (NO_2).

Found: C, 52.25; H, 6.49; N, 4.64%. Calcd for $C_{13}H_{19}NO_7$: C, 51.82; H, 6.36; N, 4.65%.

3-O-Benzyl-5,6-dideoxy-5-C-ethyl-1,2-O-isopropylidene-6-C-nitro-β-L-idofuranose (6). Hydrogenation of **5** (150 mg) in ethanol in the presence of palladium-charcoal (5%, 70 mg) at a room temperature showed the absorption of calculated amount of hydrogen (10.2 ml) within 6 min. Evaporation of the filtrate of the reaction mixture gave a sirup which was crystallized from petroleum ether. Mp 78—79 °C; $[\alpha]_D^{23}$ −50.5° (*c* 0.78, chloroform); IR: 1540 and 1374 (NO_2); NMR: 7.36 (Ph; s), 5.93 (H_1; d, $J_{1,2}$=4.0), 4.70 and 4.44 (CH_2; ABq, $J_{a,b}$=11.5), 4.66 (H_2; d), 4.47 and 4.23 (H_{6a} and H_{6b}; each q, $J_{6a,6b}$=12.5, $J_{5,6a}$=3.0, $J_{5,6b}$=6.0), 4.18 (H_4; q, $J_{3,4}$=3.0, $J_{4,5}$=8.0), 3.93 (H_3; d), 2.67 (H_5; m), 1.70—1.20 (H_7; m), 1.51 and 1.34 (2×C-CH_3), 0.97 (H_8; t, $J_{7,8}$=6.5).

Found: C, 61.57; H, 7.30; N, 3.79%. Calcd for $C_{18}H_{25}NO_6$: C, 61.52; H, 7.17; N, 3.99%.

2,4-Di-O-acetyl-3-O-benzyl-1-O-ethyl-(1,3,5/2,4,6)-6-nitro-5-vinylcyclohexanetetrol (7). A solution of **5** (0.35 g, 1 mmol) in 70% acetic acid (10 ml) was heated at 80—85 °C for 7.5 hr, evaporated to give a sirup. A solution of the sirup in ethanol (20 ml) adjusted to pH 8—9 with 2M potassium hydroxide was kept at room temperature for 2 days, neutralized with Amberlite IR-120, evaporated to give sirupy nitrocyclitol (0.28 g, 83%). Acid-catalyzed acetylation of the sirup gave the corresponding di-*O*-acetate in a quantitative yield, which was recrystallized from ethanol. Mp 146—147 °C; $[\alpha]_D^{23}$ −14.0° (*c* 0.96, chloroform). IR: 1743 and 1732 (ester), 1540 and 1368 (NO_2).

Found: C, 59.66; H, 6.40; N, 3.18%. Calcd for $C_{21}H_{27}NO_8$: C, 59.85; H, 6.46; N, 3.32%.

Intramolecular Cyclization of 3-O-Benzyl-5,6-dideoxy-6-C-nitro-5-C-vinyl-β-L-idofuranose in the Presence of Sodium Bicarbonate. A solution of a sirup obtained by de-isopropylidenation of **5** (1.91 g, 5.47 mmol), and sodium bicarbonate (60 mg) in methanol–water (each 30 ml) was kept at a room temperature for 11 hr, neutralized with Amberlite IR-120, and concentrated to give a semi-crystalline sirup which gave 3-*O*-benzyl-(3,5/1,2,4,6)-6-nitro-5-vinylcyclohexanetetrol (**8**) as crystals from ethanol. Yield, 0.88 g (52%); mp 168—169 °C; $[\alpha]_D^{23}$ −46.5° (*c* 0.99, methanol); IR: 3430, 3330, and 3190 (OH), 1548 and 1362 (NO_2), 734 and 700 (Ph).

Found: C, 58.27; H, 6.33; N, 4.38%. Calcd for $C_{15}H_{19}$-

14) D. Seyferth, "Organic Syntheses", Coll. Vol. IV, p. 258, (1963).

NO_6: C, 58.24; H, 6.19; N, 4.53%.

Acid-catalyzed acetylation of **8** (110 mg) gave quantitatively the corresponding tri-*O*-acetate (**9**) (160 mg) as a sirup which crystallized by standing for 1 month. Mp 95—96 °C; $[\alpha]_D^{23}$ −33.1° (*c* 1.01, chloroform); IR: 1740 (ester), 1550 and 1360 (NO_2).

Found: C, 58.35; H, 5.97; N, 3.09%. Calcd for $C_{21}H_{25}NO_9$: C, 57.92; H, 5.79; N, 3.22%.

On the other hand, evaporation of the mother liquor from **8** gave a sirup (0.52 g) which on acid-catalyzed acetylation gave 1,2,4-tri-*O*-acetyl-3-*O*-benzyl-(1,3,5/2,4,6)-6-nitro-5-vinylcyclohexanetetrol (**10**) as crystals which was recrystallized from ethanol. Yield, 0.7 g (34.2%); mp 165.5—166.5 °C; $[\alpha]_D^{23}$ −14.5° (*c* 1.83, chloroform); IR: 1740 (ester), 1545 and 1360 (NO_2).

Found: C, 57.66; H, 6.05; N, 3.10%. Calcd for $C_{21}H_{25}NO_9$: C, 57.92; H, 5.79; N, 3.22%.

1,2,3,4-Tetra-O-*acetyl-(1,3,5/2,4,6)-6-nitro-5-vinylcyclohexanetetrol (**11**).* De-isopropylidenation of **4** (0.34 g, 11.6 mmol) with 70% acetic acid gave a sirup (0.29 g). A solution of the sirup, and sodium bicarbonate (300 mg) in 50% methanol (20 ml) was kept at a room temperature for 1 day, neutralized with Amberlite IR-120, decolorized with charcoal, and evaporated to give a sirup (0.19 g). Acetylation of the sirup by the usual manner gave sirupy **11** (250 mg) which was crystallized from ether, and recrystallized from ethanol. Yield, 50 mg (11.4%); mp 169—170 °C; $[\alpha]_D^{23}$ −14.9° (*c* 0.74, chloroform).

Found: C, 49.57; H, 5.47; N, 3.69%. Calcd for $C_{16}H_{21}NO_{10}$: C, 49.26; H, 5.47; N, 3.62%.

*3-O-Benzyl-(3,5/1,2,4,6)-6-amino-5-ethylcyclohexanetetrol (**12**).* Hydrogenation of **8** (0.21 g) in ethanol in the presence of palladium-charcoal (110 mg, 5%) and a small amount of acetic acid for 1 day, and evaporation of the filtrate of the reaction mixture gave **12** as an acetate. Mp 203—204 °C; $[\alpha]_D^{32}$ −29.3° (*c* 1.27, methanol); IR: 3400 (OH), 3200 (NH_2) and 1680 (COOH).

Found: C, 59.80; H, 7.92; N, 4.02%. Calcd for $C_{17}H_{27}NO_6$: C, 59.81; H, 7.97; N, 4.10%.

*3-O-Benzyl-5,6,7-trideoxy-1,2-O-isopropylidene-6-C-nitro-α-D-xylo-hept-5-enofuranose (**13**).* A solution of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdose-(1,4), prepared from 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (5.0 g, 16.1 mmol) by lead tetraacetate (8 g) oxidation, and nitroethane (10 ml) in ethanol (10 ml) was adjusted to pH 9.0 with 2M potassium hydroxide, kept at a room temperature for 17 hr, neutralized with acetic acid, and then evaporated. The residual sirup was extracted with chloroform, and the extract was washed twice with water, and evaporated to give sirupy nitro alcohol (3.7 g). Acetylation of the sirup by the usual manner gave the corresponding nitro acetate (4.5 g) as a sirup. A solution of the nitro acetate (2.1 g) in benzene was refluxed for 2.5 hr in the presence of anhydrous potassium carbonate (2.8 g), and evaporation of the filtrate of the reaction mixture gave a sirup (2.0 g). Fractionation of the sirup (1.07 g) on a Kiesel Gel 60 column (20 g) with benzene–ethyl acetate (100: 3) as an effluent gave **13** (0.69 g) as a sirup. $[\alpha]_D^{23}$ −49.4° (*c* 0.93, chloroform); IR: 1520 and 1340 (conjugated NO_2). NMR: 7.31 (Ph; s), 7.18 (H_5; d, $J_{4,5}$=7.5), 6.01 (H_1; d, $J_{1,2}$=4.0), 4.82 (H_4; dd, $J_{3,4}$=3.5), 4.67 (H_2; d), 4.68 and 4.42 (CH_2; ABq, $J_{a,b}$=12.5), 3.46 (H_3; d), 2.07 (H_7; s), 1.50 and 1.33 (2× C–CH_3).

Found: C, 60.51; H, 6.31; N, 4.46%. Calcd for $C_{17}H_{21}NO_6$: C, 60.88; H, 6.31; N, 4.18%.

D-gluco-*3,4,5,6,7-Pentaacetoxy-1-nitro-1-heptene (**14**).* Acetylation of 1-*C*-nitro-1-deoxy-D-*glycero*-D-*gulo*-heptitol[11] (0.92 g, 3.8 mmol) by the usual manner gave the corresponding hexaacetate (1.88 g) as a sirup. The benzene solution of the sirup was refluxed in the presence of anhydrous potassium carbonate for 1.5 hr, filtered, and the filtrate was evaporated to give a sirup which was crystallized from ethanol. Yield, 1.10 g (77%), mp 105—106 °C; $[\alpha]_D^{23}$ +20.1° (*c* 1.16, chloroform); IR: 3090 (olefinic C–H), 1740 (ester), 1650 (C=C), 1520 and 1357 (conjugated NO_2); NMR: 7.22 (H_2; dd, $J_{1,2}$=13.0, $J_{2,3}$=5.0), 6.97 (H_1; d), 5.62 (H_3; m), 5.45—5.20 (H_4 and H_5; m), 5.03 (H_6; m), 4.23 and 4.04 (H_{7a} and H_{7b}; $J_{a,b}$=12.5, $J_{6,7a}$=3.0, $J_{6,7b}$=5.0), 2.125, 2.08, 2.05, and 2.025 (5×OAc).

Found: C, 47.26; H, 5.33; N, 3.39%. Calcd for $C_{17}H_{23}NO_{12}$: C, 47.11; H, 5.35; N, 3.23%.

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