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# C-Glycosyl Nucleosides. II.[1] Reaction of Sugar Aldehyde with Acetylenic Grignard Reagents

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Reaction of acetylenic Grignard reagents with 2,3: 4,5-di-*o*-isopropylidene-*aldehydo*-D-ribose (I) or 2,4: 3,5-di-*o*-benzylidene-*aldehydo*-D-ribose (VII) afforded 3-epimeric heptyne derivatives (II, III and VIII, IX). The configuration of these compounds was determined from nuclear magnetic resonance and mass spectra.

In previous reports, we described the reaction of ethynyl compounds with a lactone,[1] and with a glucosyl bromide[3] during attempts to obtain an intermediate for a carbon-linked nucleoside.[4,5] Horton, *et al.* already reported the ethynylation of 2,3: 4,5-di-*o*-isopropylidene-*aldehydo*-L-arabinose[6] and 2,3-*o*-isopropylidene-D-glyceraldehyde.[7]

2,3: 4,5-Di-*o*-isopropylidene-*aldehydo*-D-ribose (I), prepared through di-*o*-isopropylidene-*aldehydo*-D-ribose diethyl mercaptal by the method of English and Griswold,[8] underwent reaction with ethynylmagnesium bromide in tetrahydrofuran to give a mixture of 3-epimeric heptyne derivatives (IIa and IIIa) in a good yield. The products were detected by thin-layer chromatography (TLC) and gas chromatography. The two components (IIa and IIIa) were separated in a 3: 2 ratio by chromatography on silica gel. Both heptyne epimers (IIa and IIIa) showed the anticipated acetylenic hydrogen and C≡C stretching frequencies in their infrared (IR) spectra, at 3260 (IIa) and 3250 (IIIa), and at 2095 (IIa) and 2080 (III) $cm^{-1}$, respectively. The nuclear magnetic resonance (NMR) spectra of these compounds also showed the characteristic acetylenic hydrogen signals at $\delta$ 2.49 (IIa) and 2.48 (IIIa) ppm, respectively.

The configuration of these 3-epimeric heptynes (IIa and IIIa) was confirmed by the NMR spectra of their 3,5-dinitrobenzoates (IVa and Va). The value of $J_{3,4}$=4.6 Hz for IVa indicated the D-*altro* isomer (A) and the value of $J_{3,4}$=2.2 Hz for the other isomer (Va) indicated the D-*allo* isomer (B or B′), in analogy to observations made by Horton, *et al.*[7] for 1-pentyne-D-*erythro*-and D-*threo*-3,4,5-triol derivatives. The reaction of I with the Grignard reagent of phenyl acetylene gave mixed phenylheptyne isomers (IIb and IIIb). The configuration of these compounds was also determined from the NMR spectra of their 3,5-dinitrobenzoates IVb ($J_{3,5}$=5.0 Hz) and Vb ($J_{3,4}$=3.6 Hz). Manganese dioxide oxidation of the epimeric mixture of phenylheptynes (IIb and IIIb) yielded the 3-oxo compound (VI) which remained unchanged after treatment with diazomethane.

Reaction of ethynylmagnesium bromide with 2,4: 3,5-di-*o*-benzylidene-*aldehydo*-D-ribose (VII) gave a mixture of epimeric heptynes (VIII and IX). This mixture could only be separated by chromatography after acetylation to yield 80% of D-*allo* epimer (XI; $J_{3,1}$=2.4 Hz, $J_{3,4}$=3.3 Hz). Deacetylation of these two compounds (X and XI) with ammonia yielded

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2) Location: *Shirokane, Minato-ku, Tokyo, 108, Japan.*
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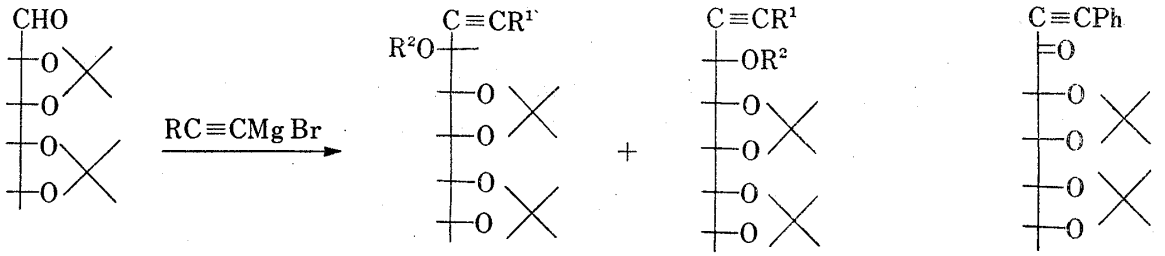
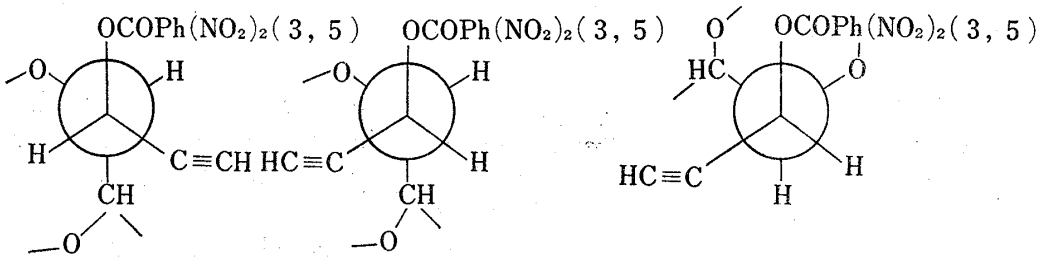



IIa : $R^1=R^2=H$ IIIa : $R^1=R^2=H$ VI

IIb : $R^1=Ph$; $R^2=H$ IIIb : $R^1=Ph$; $R^2=H$

IVa : $R^1=H$; $R^2=OOCPh(NO_2)_2(3,5)$ Va : $R^1=H$; $R^2=OOCPh(NO_2)_2(3,5)$

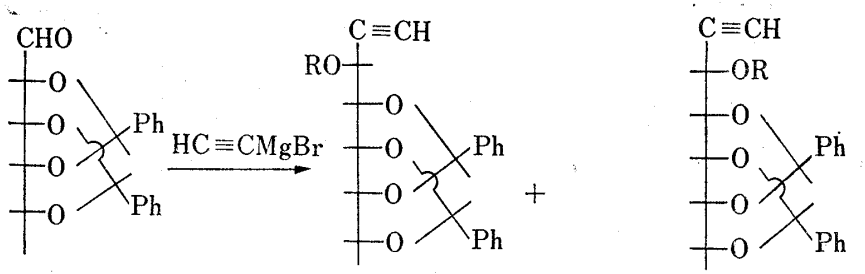
IVb : $R^1=Ph$; $R^2=OOCPh(NO_2)_2(3,5)$ Vb : $R^1=Ph$; $R^2=OOCPh(NO_2)_2(3,5)$




A B B′

ph=phenyl

Chart 1

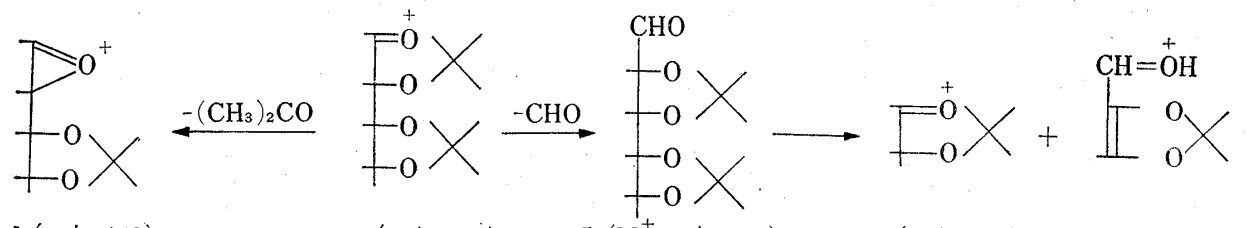



VII VIII: R=H IX: R=H

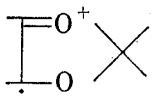
X: R=Ac XI: R=Ac

ph=phenyl

Chart 2




*d* (*m/e* 143) *c* (*m/e* 201) I ($M^+$, *m/e* 230) *a* (*m/e* 101) *b* (*m/e* 129)



*e* (*m/e* 100)

Chart 3

4,6: 5,7-di-*o*-benzylidene-1-heptyne-D-*altro*-3,4,5,6,7-pentol (VIII) and its D-*allo* isomer (IX), respectively.

In the mass spectrum of 2,3: 4,5-di-*o*-isopropylidene-*aldehydo*-D-ribose (I) the *m/e* 101 ion (*a*) is the base peak. The primary cleavage of the bond between C-3 and C-4 which produces here *m/e* 101 and *m/e* 129 (*b*), is common to all mass spectra of di-*o*-isopropylidene acetals of monosaccharides.[9] Other fragmentations are the loss of $CH_3$ to give *m/e* 215 (28%), the loss of $CH_3CO$ to give *m/e* 187 (7%), and the loss of CHO to give *m/e* 201 (*c*), from which further loss of $(CH_3)_2CO$ yields an intense peak at *m/e* 143 (*d*, 27%) (Calcd. for $C_7H_{11}O_3$: 143.071. Found: 143.071). Loss of the ion *a* from the ion *c* gives an ion *e* (*m/e* 100).

The mass spectra of the ethynyl compounds shown similar fragmentations. IIa and IIIa show strong peaks at *m/e* 241 (57% and 44%, respectively) owing to M-$CH_3$ ion and the ion *a* (*m/e* 101; 100% and 95%, respectively) from cleavage of the bond between C-5 and C-6. M-$C_3H_3O$ (*c*, *m/e*; 8% and 7%, respectively) and *m/e* 143 ions (*d*; 41% and 100%, respectively) are also observed from cleavage of the bond between C-3 and C-4.

In the case of the phenylethynyl compounds (IIb and IIIb), the *d* ion is the base peak, and the intensities of *c* ion (0% and 18%, respectively) correspond to the difference between IIa and IIIa. This fact suggests a difference in the configuration of the hydroxyl group at C-3.

## Experimental

Melting points and boiling points are uncorrected. Infrared spectra were recorded with a Shimadzu IR 27G spectrometer. Optical rotations were determined with a JASCO DIP-SL automatic polarimeter. Circular dichroism and optical rotatory dispersion curves were determined with a JASCO J-20 in MeOH, gas chromatographs with a flame ionization detector, using a 2.7 mm×3 m column of 15% polydiethylene glycol succinate on Chromosorb W (60—80 mesh). NMR spectra were measured with a Varian T-60 and a JEOL PS-100 spectrometer with tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL JMS-OlS spectrometer by a direct inlet system at 75 eV.

**2,3: 4,5-Di-*o*-isopropylidene-*aldehydo*-D-ribose (I)**——This compound was prepared by the procedure of English and Griswold.[8] Colorless liquid, bp 92—93° (0.1 mm) (reported, bp 73—75° (0.1 mm).[10] IR $\nu_{max}^{film}$ $cm^{-1}$: 2835 and 2730 (CHO), 1732 (CO), 1378 and 1370 ($CMe_2$), 1215, 1155, and 1060 (oxide). Mass Spectrum *m/e* (relative intensity): 230 $M^+$ (0.7), 215 (28), 201 (7), 187 (7), 171 (23), 157 (16), 143 (27), 101 (100), 85 (24), 59 (53), 43 (60).

***p*-Nitrophenylhydrazone**: Yellow prisms (from 60% EtOH), mp 195—197°. *Anal.* Calcd. for $C_{17}H_{23}O_6N_3$: C, 55.88; H, 6.35; N, 11.50. Found: C, 55.59; H, 6.25; N, 11.31.

**4,5: 6,7-Di-*o*-isopropylidene-1-heptyne-D-*altro*- (IIa) and -D-*allo*-3,4,5,6,7-pentol (IIIa)**——A solution of ethylmagnesium bromide prepared from magnesium (2.0 g) and ethyl bromide (8 ml) in anhydrous tetrahydrofuran (120 ml), was added dropwise to tetrahydrofuran (210 ml) saturated with acetylene at room temperature. A stream of acetylene was passed through the solution during the addition, and for 1 hr afterwards. To the resulting pink solution, freshly distilled I (8.3 g) in tetrahydrofuran (50 ml) was added dropwise with stirring at room temperature. A slow stream of acetylene was passed through the solution during this addition and subsequently for further 4 hr. The reaction solution was decomposed with $NH_4Cl$ solution (400 ml) at 0° and extracted with ether. Evaporation of the dried ($Na_2SO_4$) solution left a syrup (6.7 g), composed of two epimeric heptynes as detected by TLC and GLC. The syrup was separated on GLC to obtain IIa and IIIa in a ratio of about 3: 2. There was also obtained a small amount of another two isomers having the same $M^+$ (*m/e*: 256). D-*Altro* compound (IIa) showed mp 72—73° from EtOH. TLC: *Rf* 0.62 (benzene–MeOH, 4: 1). GLC: 6.2 min ($N_2$, 13 ml/min, 169°). $[\alpha]_D^{23}$ −21.0° (*c*=1.1, $CHCl_3$). $[\theta]_{215}^{22}$ −273, $[\theta]_{246}$ 0, $[\theta]_{260}$ +31 (MeOH). *Anal.* Calcd. for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 60.66; H, 7.96. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3545 (OH), 3260 (≡CH), 2095 (C≡C), 1382 and 1372 ($CMe_2$). UV $\lambda_{max}^{EtOH}$ nm (log ε): 260 (2.62). NMR δ (ppm): 1.34, 1.38, 1.39 and 1.47 (12H, singlet, $CMe_2$), 2.49 (1H, doublet, $J_{1,3}$=2.2 Hz, ≡CH), 3.32 (1H, doublet, $J_{H,OH}$=

9) N.K. Kochetkov and O.S. Chizhov, "Advances in Carbohydrate Chemistry," Vol. 21, Ed. by M.L. Wolfrom, 1966, p. 39. Academic Press, New York, and references cited therein.

10) M.A. Bukhari, A.B. Foster, J. Lehmann, J.M. Webber, and J.H. Westwood, *J. Chem. Soc.*, 2291 (1963). The thioketal of I was a mixture of two components having the same molecular peak (*m/e* 336 $M^+$) as detected by gas–liquid chromatography (GLC). Confirmation of the structure will appear in the near future.

9.4 Hz, OH, disappeared on addition of $D_2O$), 3.60—4.87 (6H, multiplet, 3,4,5,6,7-H). Mass Spectrum *m/e*: 256 $M^+$ (0.9), 241 (57), 201 (8). 143 (41), 101 (100), 59 (71), 43 (61).

D-*Allo* compound (IIIa). Colorless syrup. TLC: *Rf* 0.53 (benzene–MeOH, 4: 1). GLC: 8 min ($N_2$, 13 ml/min, 169°). $[\alpha]_D^{23}$ −27.8° (*c*=0.9, $CHCl_3$). $[\theta]_{210}^{22}$ −1036, $[\theta]_{310}$ −193. *Anal.* Calcd. for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 60.63; H, 7.96. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3485 (OH), 3250 (≡CH), 2080 (C≡C), 1384 and 1370 ($CMe_2$). NMR ($CDCl_3$, 60 MHz) $\delta$ (ppm): 1.33, 1.37, 1.38 and 1.49 (12H, singlet, $CMe_2$), 2.48 (1H, doublet, $J_{1,3}$=2.3 Hz, ≡CH), 2.75 (1H, doublet, $J_{H,OH}$=9.1 Hz, OH, disappeared on addition of $D_2O$), 3.50—4.31 (5H, multiplet, 4,5,6,7-H), 4.61 (1H, broad quartet, 3-H). UV $\lambda_{max}^{EtOH}$ nm (log $\varepsilon$): 258.6 (2.58). Mass spectrum *m/e*: 256 $M^+$ (1.3), 241 (44), 201 (7), 183 (7), 143 (100), 101 (95), 85 (24), 59 (64), 43 (88).

**3-*o*-(3,5-Dinitrobenzoyl)-4,5: 6,7-di-*o*-isopropylidene-1-heptyne-D-*altro*-3,4,5,6,7-pentol (IVa)**——A solution of IIa (0.5 g) and 3,5-dinitrobenzoyl chloride (1 g) in pyridine (8 ml) containing benzene (10 ml) was kept overnight at room temperature. The solution was poured into ice-water and this was extracted with ether. The dried ether solution was evaporated to leave a solid (0.8 g, 92%). The product was recrystallized from EtOH to give II as pale yellow needles, mp 158—160°. $[\alpha]_D^{25}$ +45.5° (*c*=0.9, $CHCl_3$). *Anal.* Calcd. for $C_{20}H_{22}O_{10}N_2$: C, 53.33; H, 4.92; N, 6.22. Found: C, 53.63; H, 5.12; N, 6.15. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3290 (≡CH), 2120 (C≡C), 1734 (CO), 1543 ($NO_2$), 1384 and 1373 ($CMe_2$). NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm): 1.22, 1.39, 1.40, and 1.57 (12H, singlet, $CMe_2$), 2.63 (1H, doublet, $J_{1,3}$=2.1 Hz, ≡CH), 3.70—4.40 (multiplet, 4,5,-6,7-H), 4.40—4.80 (1H, multiplet, 4-H), 5.95 (1H, quartet, $J_{3,1}$=2.1 Hz, $J_{3,4}$=4.6 Hz, 3-H), 9.18 (3H, singlet, aromatic protons). Mass Spectrum *m/e*: 435 ($M^+$-$CH_3$) (10), 377 (9), 195 (26), 181 (11), 157 (41), 143 (15), 114 (35), 101 (40), 69 (55), 59 (89), 43 (100).

**3-*o*-(3,5-Dinitrobenzoyl)-4,5: 6,7-di-*o*-isopropylidene-1-heptyne-D-*allo*-3,4,5,6,7-pentol (Va)**——The *allo* compound (IIIa; 0.5 g) was treated with 3,5-dinitrobenzoyl chloride as described for the *altro* isomer. Recrystallization from EtOH gave Va (0.85 g, 93%) as colorless needles, mp 197—198°. $[\alpha]_D^{25}$ +38.4° (*c*=1, $CHCl_3$). *Anal.* Calcd. for $C_{20}H_{22}O_{10}N_2$: C, 53.33; H, 4.92; N, 6.22. Found: C, 53.40; H, 5.03; N, 6.33. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3275 (≡CH), 2100 (C≡C), 1727 (CO), 1547 ($NO_2$), 1381 and 1373 ($CMe_2$). NMR ($CDCl_3$, 100 MHz) $\delta$ (ppm): 1.35, 1.48, 1.49 and 1.52 (12H, singlet, $CMe_2$), 2.62 (1H, doublet, $J_{1,3}$=2.3 Hz, ≡CH), 3.90—4.32 (5H, multiplet, 4,5,6,7-H), 5.92 (1H, triplet, $J_{3,1}$=2.3 Hz, $J_{3,4}$=2.2 Hz, 3-H), 9.24 (3H, singlet, aromatic protons). Mass Spectrum *m/e*: 435 ($M^+$-$CH_3$) (14), 195 (32), 157 (69), 114 (37), 59 (100), 43 (50).

**4,5: 6,7-Di-*o*-isopropylidene-1-phenyl-1-heptyne-D-*altro*- (IIb) and -D-*allo*-3,4,5,6,7-pentol (IIIb)**——A solution of phenylacetylene (4.2 g) in anhydrous ether (30 ml) was added to isopropylmagnesium bromide, prepared from isopropyl bromide (5.1 g) and magnesium (0.9 g) in ether (40 ml). This solution of phenylethynylmagnesium bromide was warmed under reflux for 30 min, cooled, and freshly distilled I (3 g) in ether (30 ml) was added dropwise during 30 min. The mixture was stirred for 4 hr at room temperature, and a yellow precipitate was produced. The reaction mixture was treated with $NH_4Cl$ solution and extracted with ether. The ether solution was dried ($Na_2SO_4$) and evaporated to give a mixture of epimers (IIb and IIIb) as a yellowish brown syrup (3.6 g). The product was chromatographed on silica gel. Elution with benzene gave IIb (0.8 g, 19%). Elution with benzene–acetone (49: 1) afforded IIIb (2.1 g, 50%). The D-*altro* compound (IIb) did not crystallize even after chromatography on silica gel. TLC: *Rf* 0.66 (benzene–acetone, 5: 1). $[\alpha]_D^{25}$ −3.1° (*c*=1.4, $CHCl_3$). *Anal.* Calcd. for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 68.35; H, 7.46. IR $\nu_{max}^{film}$ $cm^{-1}$: 3450 (OH), 2185 (C≡C), 1379 and 1370 ($CMe_2$). NMR ($CCl_4$, 60 MHz) $\delta$ (ppm): 1.18, 1.19, 1.22, and 1.26 (12H, singlet, $CMe_2$), 1.84 (1H, broad singlet, OH), 3.51—4.88 (6H, multiplet, 3,4,5,6,7-H), 6.79—7.62 (5H, multiplet, aromatic protons). Mass Spectrum *m/e*: 332 $M^+$ (2), 317 (16), 274 (6), 220 (10), 202 (32), 173 (13), 143 (100), 129 (62), 101 (35), 43 (63).

D-*Allo* Compound (IIIb): Colorless needles mp 134—135° (MeOH–$H_2O$). *Anal.* Calcd. for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 68.92; H, 7.51. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3475 (OH), 2215 (C≡C), 1390 and 1383 ($CMe_2$). NMR ($CCl_4$, 60 MHz) $\delta$ (ppm): 1.33, 1.40, 1.41, and 1.51 (12H, singlet, $CMe_2$), 2.42 (1H, broad singlet, OH), 3.61—4.40 (5H, multiplet, 4,5,6,7-H), 4.62 (1H, multiplet, 3-H), 7.01—7.61 (5H, multiplet, aromatic protons). Mass Spectrum *m/e*: 332 $M^+$ (32), 317 (9), 274 (3), 259 (6), 201 (18), 187 (17), 173 (8), 157 (16), 143 (100), 131 (26), 101 (5), 77 (8), 59 (32), 43 (28).

**3-*o*-(3,5-Dinitrobenzoyl)-4,5: 6,7-di-*o*-isopropylidene-1-phenyl-1-heptyne-D-*altro*-3,4,5,6,7-pentol (IVb)**——Compound IIb (1.8 g) was treated with 3,5-dinitrobenzoyl chloride (2 g) and pyridine (20 ml) as described under IVa. The product was obtained as a colorless powder (2.5 g, 90%), mp 165—167° (MeOH). TLC: *Rf* 0.61 (benzene–acetone, 5: 1). $[\alpha]_D^{23}$ −28.5° (*c*=1.3, $CHCl_3$). $[\theta]_{216}^{20}$ +4855, $[\theta]_{238}$ −1828, $[\theta]_{285}$ −928, $[\theta]_{320}$ −503. *Anal.* Calcd. for $C_{26}H_{26}O_{10}N_2$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.58; H, 4.93; N, 5.07. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 2220 (C≡C), 1735 (CO), 1383 and 1374 ($CMe_2$). NMR ($CCl_4$, 60 MHz) $\delta$ (ppm): 1.21, 1.40, 1.42, and 1.58 (12H, singlet, $CMe_2$), 3.60—4.75 (5H, multiplet, 4.5,6,7-H), 6.08 (1H, doublet, $J_{3,4}$= 5.0 Hz, 3-H), 7.15 (5H, multiplet, aromatic protons), 9.40 (3H, singlet, $C_6H_3(NO_2)_2$). Mass Spectrum *m/e*: 526 $M^+$ (5), 511 (9), 453 (5), 439 (5), 426 (5), 393 (5), 257 (15), 195 (62), 143 (100), 101 (94), 43 (85).

**3-*o*-(3,5-Dinitrobenzoyl)4,5: 6,7-di-*o*-isopropylidene-1-phenyl-1-heptyne-D-*allo*-3,4,5,6,7-pentol (Vb)**——Compound IIIb (0.66 g) was treated with 3,5-dinitrobenzoyl chloride (1 g) by the same procedure as described under IVa. The product (Vb) was obtained as a colorless powder (0.86 g, 87%) mp 145°. TLC: *Rf* 0.7 (benzene–acetone, 5: 1). $[\alpha]_D^{23}$ −37.0° (*c*=1.6, $CHCl_3$). $[\theta]_{216}^{20}$ +4092, $[\theta]_{226}$ 0, $[\theta]_{240}$ −7404, $[\theta]_{286}$ −678, $[\theta]_{328}$ −477. *Anal.* Calcd. for $C_{26}H_{26}O_{10}N_2$: C 59.31; H, 4.98; N, 5.32. Found: C, 59.07; H, 4.89;

N, 5.55. IR $\nu_{max}^{film}$ cm$^{-1}$: 2220 (C≡C), 1738 (CO), 1380 and 1370 ($CMe_2$). NMR ($CCl_4$, 60 MHz) $\delta$ (ppm): 1.38, 1.39, 1.51, and 1.52 (12H, singlet, $CMe_2$), 3.80—4.35 (5H, multiplet, 4,5,6,7-H), 6.08 (1H, doublet, $J_{3,4}$= 3.6 Hz, 3-H), 7.30 (5H, multiplet, aromatic protons), 9.42 (3H, singlet, $C_6H_3(NO_2)_2$). Mass spectrum *m/e*: 526 M$^+$ (6), 511 (1), 453 (1), 393 (2), 195 (27), 143 (57), 101 (14), 59 (88), 43 (100).

**4,5: 6,7-Di-*o*-isopropylidene-3-oxo-1-phenyl-1-heptyne-D-ribo-4,5,6,7-tetraol (VI)**——Active manganese dioxide (1 g) was added to the solution of the epimeric mixture of heptynes (IIb and IIIb; 0.1 g) in $CHCl_3$ (10 ml). The mixture was stirred for 5 hr at 20° and the resulting filtrate was evaporated to yield VI (0.06 g, 60%) as yellow prisms, mp 65—72°. $[\alpha]_D^{22}$ −8.9° (*c*=1.1, $CHCl_3$). *Anal.* Calcd. for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 69.31; H, 6.88. IR $\nu_{max}^{film}$ cm$^{-1}$: 2180 (C≡C), 1675 (CO), 1382 and 1375 ($CMe_2$). NMR ($CDCl_3$, 60 MHz) $\delta$ (ppm): 1.30, 1.42, 1.60, and 1.67 (12H, singlet, $CMe_2$), 3.76—4.88 (5H, multiplet, 4,5,6,7-H), 7.24—7.80 (5H, multiplet, aromatic protons). Mass Spectrum *m/e*: 330 M$^+$ (4), 315 (8), 257 (6), 201 (8), 171 (15), 143 (100), 129 (72), 115 (27), 101 (33), 85 (31), 59 (52), 43 (99).

**Benzylidene-*aldehydo*-D-ribose (VII)**——This compound was prepared by the procedure of Zinner and Wittenburg.[11]

*p*-Nitrophenylhydrazone: Pale yellow fine needles (from DMSO), mp 258°. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3170 (NH), 1600, 750, 685 (phenyl). NMR (DMSO-$d_6$, 60 MHz) $\delta$ (ppm): 5.80, 6.00 (2H, singlet, -CH-), 7.24—7.60 (10H, multiplet, aromatic protons), 7.10, 8.10 (4H, doublet, $C_6H_4NO_2$), 10.6 (1H, singlet, NH). Mass Spectrum *m/e*: M$^+$ Calcd. for $C_{25}H_{23}O_6N_3$: 461.159. Found: 461.159.

**4,6: 5,7-Di-*o*-benzylidene-1-heptyne-D-*altro*- (VIII) and -D-*allo*-3,4,5,6,7-pentol (IX) Mixture**——To the solution of ethynylmagnesium bromide (0.028 mole), a solution of 2,4: 3,5-di-*o*-benzylidene-*aldehydo*-D-ribose (VII; 1.7 g, 0.0052 mole) in tetrahydrofuran (100 ml) was added dropwise during 1 hr, and the reaction mixture was stirred at room temperature for 7 hr. After the same treatment of the reaction mixture as in the preparation of IIa and IIIa, a mixture of crude VIII and IX was obtained as a yellow powder (2.2 g). The product was chromatographed on silica gel but the two epimers could not be separated. The mixture was obtained as a colorless crystalline powder from MeOH, mp 160—170°. *Anal.* Calcd. for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.80; H, 5.60. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3455 (OH), 3300 (≡CH), 2100 (C≡C), 1622 (arom). NMR ($CDCl_3$, 60 MHz) $\delta$ (ppm): 2.39 and 2.47 (1H, doublet, $J_{1,3}$=2.4 Hz, ≡CH), 2.66 (1H, doublet, $J_{H,OH}$= 3.9 Hz, OH, disappeared on addition of $D_2O$), 3.39—4.40 (6H, multiplet, 3,4,5,6,7-H), 5.6 and 5.74 (1H, singlet, $ArCHO_2$), 7.15—7.65 (10H, broad singlet, $(C_6H_5)_2$). Mass Spectrum *m/e*: 352 M$^+$ (1), 297 (38), 203 (22), 191 (34), 149 (100), 145 (35), 107 (81), 105 (81), 91 (80), 79 (73), 77 (65), 55 (13).

**3-*o*-Acetyl-4,6: 5,7-di-*o*-benzylidene-1-heptyne-D-*altro*- (X) and -D-*allo*-3,4,5,6,7-pentol (XI)**——A solution of the mixture of epimers (VIII and IX, 3 g) in pyridine (10 ml) and acetic anhydride (18 ml) was left for 48 hr at room temperature. The mixture was poured into water, and which was extracted with $CHCl_3$. The dried ($Mg_2SO_4$) $CHCl_3$ solution was evaporated to give a mixture of the 3-acetates (X and XI) as a colorless solid (2.9 g, 90%). Recrystallization from EtOH gave the pure D-*allo* epimer (XI) as colorless needles (2.3 g, 80%), mp 168—170°. $[\alpha]_D^{23}$ −82.6° (*c*=1.2, $CHCl_3$). $[\phi]_{218}^{20}$ −4528. *Anal.* Calcd. for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 69.84; H, 5.89. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3285 (≡CH), 2110 (C≡C), 1741 (CO), 1450 and 1380 ($CH_3$). NMR ($C_6D_6$, 100 MHz) $\delta$ (ppm): 1.14 (3H, singlet, OAc), 2.06 (1H, doublet, $J_{1,3}$=2.4 Hz, ≡CH), 3.41—4.39 (5H, multiplet, 4,5,6,7-H), 5.38 and 5.41 (1H, singlet, $CHO_2$), 6.16 (1H, triplet, $J_{3,1}$=2.4 Hz, $J_{3,4}$=2.6 Hz, 3-H), 7.63 (10H, multiplet, aromatic protons). Mass Spectrum *m/e*: 394 M$^+$ (2), 297 (8), 288 (2), 245 (6), 191 (6), 139 (23), 106 (18), 105 (77), 91 (59), 79 (22), 77 (28), 51 (9), 43 (100).

Several recrystallizations from EtOH of crude D-*altro* epimer, which was obtained from the mother liquor, gave D-*altro* epimer (X, 0.58 g, 20%) as colorless leaflets, mp 133—135°. $[\alpha]_D^{23}$ −37.3° (*c*=1.0, $CHCl_3$). $[\phi]_{210}^{20}$ −4442. *Anal.* Calcd. for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 69.76; H, 5.69. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3275 (≡CH), 2105 (C≡C), 1737 (CO), 1451 and 1374 ($CH_3$). NMR ($C_6D_6$, 100 MHz) $\delta$ (ppm): 1.62 (3H, singlet, OAc), 2.22 (1H, doublet, $J_{1,3}$=2.3 Hz, ≡CH), 3.40—4.40 (5H, multiplet, 4,5,6,7-H), 5.38 and 5.44 (1H, singlet, $CHO_2$), 6.07 (1H, triplet, $J_{3,1}$=2.3 Hz, $J_{3,4}$=3.3 Hz, 3-H), 7.57 (10H, multiplet, aromatic protons). Mass Spectrum *m/e*: 394 M$^+$ (5), 297 (18), 288 (7), 245 (15), 191 (16), 139 (19), 106 (30), 105 (90), 91 (24), 79 (16), 77 (45), 51 (14), 43 (100).

**4,6: 5,7-Di-*o*-benzylidene-1-heptyne-D-*altro*-3,4,5,6,7-pentol (VIII) from X**——A suspension of X (0.1 g) in MeOH (22 ml) was saturated with $NH_3$ at 0° for 20 min until the mixture became a clear solution. Evaporation of the solution gave VIII as a colorless powder (0.045 g), which recrystallized from EtOH to fine colorless needles, mp 132—134°. $[\alpha]_D^{20}$ −66.5° (*c*=0.7, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.25; H, 5.50. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3350 (OH), 3310 (≡CH), 2090 (C≡C), 1625 (arom). NMR ($CDCl_3$, 60 MHz) $\delta$ (ppm): 2.54 (1H, doublet, $J_{1,3}$=2.6 Hz, ≡CH), 2.75 (1H, broad doublet, OH, disappeared on addition of $D_2O$), 3.62—4.52 (5H, multiplet, 4,5,6,7-H), 4.52—4.93 (1H, multiplet, 3-H), 5.65 and 5.73 (1H, singlet, $CHO_2$), 7.20—7.71 (10H, multiplet, aromatic protons).

**4,6: 5,7-Di-*o*-benzylidene-1-heptyne-D-*allo*-3,4,5,6,7-pentol (IX) from XI**——XI (0.243 g) was treated by the same procedure as described above. IX was obtained as a colorless powder (0.10 g), which was recrystallized from EtOH–acetone (5: 1) to give fine colorless needles, mp 186—187°. $[\alpha]_D^{20}$ −64.3° (*c*=0.7, $CHCl_3$).

11) H. Zinner and E. Wittenburg, *Chem. Ber.*, **94**, 1298 (1961).

*Anal.* Calcd. for $C_{21}H_{20}O_5$: C, 71.58; H, 5.72. Found: C, 71.22; H, 5.60. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3510 (OH), 3300 (≡CH), 2085 (C≡C), 1620 (arom). NMR ($CDCl_3$, 60 MHz) $\delta$ (ppm): 2.49 (1H, doublet, $J_{1,3}$=2.4 Hz, ≡CH), 2.66 (1H, multiplet, OH), 3.70—4.54 (5H, multiplet, 4,5,6,7-H), 4.54—4.90 (1H, multiplet, 3-H), 5.70 and 5.84 (1H, singlet, $CHO_2$), 7.20—7.64 (10H, multiplet, aromatic protons).

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