Carbohydrate Research, 75 (1979) 141–150

CONVERSION OF ω-TERMINAL-ACETYLENIC SUGAR DERIVATIVES INTO ACETYLENIC GLYCOSIDES AND NUCLEOSIDES, AND FORMATION OF "DOUBLE-HEADED NUCLEOSIDE" ANALOGS*

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(Received February 5th, 1979; accepted for publication, February 20th, 1979)

ABSTRACT

3,5-Di-*O*-acetyl-6,7-dideoxy-1,2-*O*-isopropylidene-β-L-*ido*- and -α-D-*gluco*-hept-6-ynofuranose were separately deacetonated, and the products acetylated, to give the 1,2,3,5-tetra-*O*-acetyl analogs (**2** and **6**). Fusion of compounds **2** and **6** with 2,6-dichloropurine under acid catalysis produced 2,6-dichloro-9-(2,3,5-tri-*O*-acetyl-6,7-dideoxy-α-L-*ido*-hept-6-ynofuranosyl)-9*H*-purine (**3**) and its β-D-*gluco* analog **7**, respectively. Methanolic ammonia converted **3** in good yield into 2-chloro-9-(6,7-dideoxy-α-L-*ido*-hept-6-ynofuranosyl)-6-methoxy-9*H*-purine. Treatment of compound **3** with mesityl nitrile oxide gave a "double-headed nucleoside" analog. Upon treatment with phenyl azide, the D-*gluco* derivative **7** produced another "double-headed nucleoside". Fusion of **2** and **6** with *p*-nitrophenol yielded the respective *p*-nitrophenyl glycosides. The stereochemistry and regiospecificity of the reactions were verified spectroscopically.

INTRODUCTION

The potential of acetylenic sugar derivatives as useful, synthetic intermediates has been under general evaluation in this laboratory[1–3]. As nucleoside analogs, both natural[4–9] and synthetic[9,10], containing unsaturated functionality in the sugar portion have displayed pharmacological potential as antibacterial agents, it was of interest to evaluate the feasibility of nucleoside coupling-reactions in sugar derivatives containing the acetylenic group. The previously demonstrated[11] stability, and stereochemical integrity, of the propargylic alcohol function in a carbohydrate system under the mild acid or base conditions used in many transformations of sugars is an attractive feature for numerous, synthetic applications[3]. Although such functionality was not expected to survive the conventional conditions for the production of glycosyl

*Part XVIII of the series "Extension of Sugar Chains Through Acetylenic Intermediates". For Part XVII, see ref. 1. This investigation was supported, in part, by the National Institute of General Medical Sciences, National Institutes of Health, U. S. Public Health Service, Grant No. GM-11976 (The Ohio State University Research Foundation Project 711049). For a preliminary report, see ref. 2.

halides as a route to nucleosides or glycosides, the possibility of using the fusion technique, starting from an acetate precursor, appeared more feasible; the successful application of this reaction with 2,6-dichloropurine for the generation of ω'-terminal acetylenic nucleoside analogs and (with *p*-nitrophenol) aryl glycosides is the subject of this paper. Also described are examples whereby the ethynyl function of the ω'-acetylenic nucleosides is subsequently subjected to 1,3-dipolar cycloaddition to give "double-headed nucleoside" analogs having a purine at C-1 and a *C*-linked heterocycle at C-4 of a furanoid sugar-ring.

DISCUSSION

The starting material in the L-*ido* series, 1,2,3,5-tetra-*O*-acetyl-6,7-dideoxy-α-(and β)-L-*ido*-hept-6-ynofuranose (**2**), was prepared as a syrupy, anomeric mixture by sequential deacetonation[12] and acetylation of 3,5-di-*O*-acetyl-6,7-dideoxy-1,2-*O*-isopropylidene-β-L-*ido*-hept-6-ynofuranose[3] (**1**). The base-coupling was performed according to the general, fusion technique of Montgomery and Hewson[13]; the anomeric mixture of peracetylated, acetylenic sugar derivatives **2** was fused at 140° with 2,6-dichloropurine in the presence of a catalytic amount of *p*-toluenesulfonic acid until acetic acid ceased to be evolved. The syrupy product was resolved by preparative t.l.c., to give the crystalline α-L anomer **3**. The D-*gluco* acetylenic nucleoside analog was obtained by the same sequence from the corresponding D-*gluco* precursors **5** (ref. 3) and **6**, and the crystalline product **7** was obtained.

Both 5-epimeric, acetylenic nucleoside analogs showed infrared absorptions at 3.05 and 4.68 μm characteristic of the C–H and C≡C bonds of the terminal acetylenic group (C≡C—H). A strong carbonyl absorption, from the acetyl group, appeared at 5.68 μm for the L-*ido* isomer and at 5.74 μm for the D-*gluco* isomer. Absorptions at 6.25, 6.40, and 6.68 μm were indicative[14] of the purine moiety.

The 100-MHz, ^{1}H-n.m.r. spectra (see Tables I and II) of the coupled products (**3** and **7**) verified the presence of several functional groups in the products of the fusion reaction. The assignment of chemical shifts was confirmed by spin decoupling.

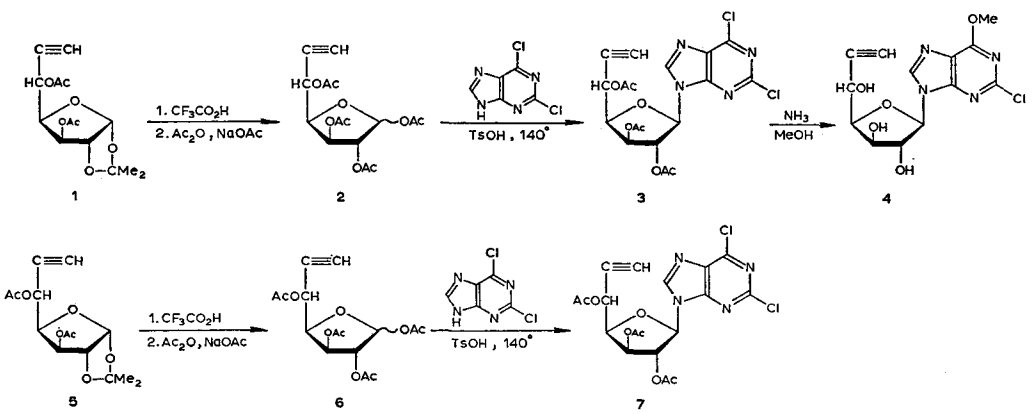


TABLE I

CHEMICAL SHIFTS OF PROTONS

Compound	*Solvent*	*Chemical shifts (δ) from 100-MHz spectra*[a]							
		H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-7*	*Ar*	*Other*
3	$CDCl_3$	6.30d	5.55dd	5.65dd	4.70dd	5.80dd	2.59d	8.58s (purine)	2.21 (OAc) 2.13 (2)(OAc)
4	acetone-d_6[b]	5.99d	4.26			5.34m	2.79d	8.41s (purine)	4.05s ($-OCH_3$)
7	$CDCl_3$	6.37d	5.42dd	5.56dd	4.58dd	5.70dd	2.58d	8.59s (purine)	2.19 (OAc) 2.12 (OAc) 2.10 (OAc)
8	$CDCl_3$	6.26d	5.64dd	5.53dd	5.11dd	6.43d		6.89s(Ph) 6.27s (hetero) 8.50s (purine)	2.30 2.16 (2) 2.07 (3) (OAc and Ar-CH_3)
9	$CDCl_3$	6.24d	5.46dd	5.79dd	5.33dd	6.29d		7.43–7.77(Ph) 8.08s (hetero) 8.38s (purine)	2.21 (OAc) 2.12 (OAc) 2.02 (OAc)
10	$CDCl_3$	5.73s	5.36d	5.58dd	4.73dd	5.55dd	2.48d	7.16–8.24	2.16 (OAc) 2.00 (2)(OAc)
11	$CDCl_3$	5.72s	5.39d	5.54dd	4.71dd	5.57dd	2.39d	7.08–8.24	2.14 (OAc) 2.10 (OAc) 2.02 (OAc)

[a]First-order values are given. Observed multiplicities: d, doublet; dd, doublet of doublets; m, multiplet; s, singlet. [b]Under proton–deuterium exchange, the OH or NH signal disappears.

TABLE II

FIRST-ORDER, PROTON–PROTON COUPLING-CONSTANTS

Compound	*Solvent*	*Coupling constants (Hz) from 100-MHz spectra*				
		$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,7}$
3	$CDCl_3$	2.5	2.5	4.5	7.0	2.0
4	acetone-d_6[a]	2.0				2.0
7	$CDCl_3$	2.0	1.5	4.0	6.5	2.5
8	$CDCl_3$	2.5	3.0	5.0	6.5	
9	$CDCl_3$	1.5	2.0	4.0	9.0	
10	$CDCl_3$	<0.3	1.6	5.5	7.8	2.0
11	$CDCl_3$	<0.3	1.7	5.5	8.0	2.2

[a]Spectra were simplified by proton–deuterium exchange.

The purine proton (H-8) resonated as a low-field singlet at δ 8.58 for the L-*ido* isomer **3** and δ 8.59 for the D-*gluco* isomer **7**. Analysis of the spectra showed the expected, narrow, high-field doublet for the acetylenic proton, at δ 2.59 for the L-*ido* isomer and 2.58 for the D-*gluco* isomer, displaying $J_{5',7'}$ values of 2.0 and 2.5 Hz, respectively. The spectrum of the L-*ido* isomer **3** showed the acetyl methyl proton resonances as two singlets at δ 2.21 and 2.13. Integration of these peak areas corresponded to three and six protons each. The D-*gluco* isomer **7** showed three, 3-proton singlets in the same region. These signals may be attributed to the acetyl methyl protons. The ring protons of the sugar moiety resonated as apparent doublets of doublets, and corresponded well with a preceding example of a nucleoside containing this same ring-system[15]. The anomeric proton resonated as a doublet at low field (L-*ido*, δ 6.30; D-*gluco*, δ 6.37). The signals showed small spin-coupling with H-2 (L-*ido* isomer, 2.5 Hz; D-*gluco* isomer, 2.0 Hz). The magnitude of $J_{1',2'}$ is consistent with the values obtained in previous work on glycofuranosylpurine nucleosides having a furanoid ring of the *xylo* configuration[15,16], in which a $J_{1,2}$ value of ~2.0 Hz was observed[15] for 1,2-*trans*-coupled protons, in contrast to a $J_{1,2}$ value for 1,2-*cis*-coupling of ~4.0 Hz. Favored formation of the α-L product was to be anticipated from the C-1–C-2 *trans* rule[17,18], through anchimeric assistance[17,18] of the 2-acyloxyl group.

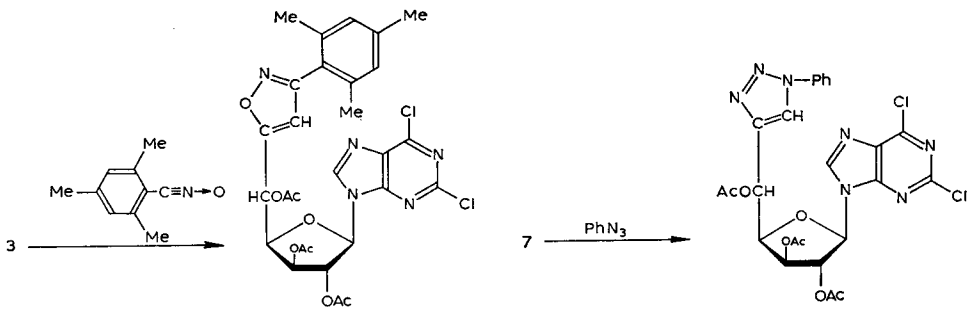
It has been demonstrated previously[11], for other acetylenic-sugar systems, that the propargylic hydroxyl group is not epimerized by acid or base under the conventional conditions of glycoside hydrolysis or saponification of acyl groups. By analogy, it may be anticipated that the stereochemistry at the propargylic position is unchanged throughout the sequences of nucleoside synthesis **1**–**3** and **5**–**7**, and the differences in $[\alpha]_D$ and n.m.r.-spectral parameters for **3** and **7** bear this out.

Under anhydrous conditions, the protected nucleoside **3** was deacetylated with methanolic ammonia overnight at 0°, and the recrystallized product was obtained as needles in 69% yield. It was formulated as 2-chloro-9-(6,7-dideoxy-α-L-*ido*-hept-

6-ynofuranosyl)-6-methoxy-9*H*-purine (**4**) on the basis of analytical and spectroscopic evidence. Its mass spectrum showed a peak at *m/e* 340 for the molecule-ion, together with fragmentation products at 213 (baseH$^+$-CH=O), 199, 198, 184 (H-base$^+$), and 183, as expected for a substituted-purine nucleoside derivative. The i.r. spectrum of **4** showed absorption for the hydroxyl group, and the absorptions observed at 3.05 and 4.70 μm were assigned to the terminal acetylenic group; other absorptions could be attributed to the purine moiety.

The 100-MHz, ^{1}H-n.m.r. spectrum of **4** in acetone-d_6, after proton–deuterium exchange, displayed the resonance of the purine proton as a low-field singlet (at δ 8.41), and the anomeric-proton resonance as a doublet at δ 5.99 ($J_{1,2}$ 2.0 Hz). The high-field doublet at δ 2.79 is characteristic of the acetylenic proton. A 3-proton singlet at δ 4.05 is attributable to the methoxyl group. The u.v. spectrum of **4** showed strong absorption at 257 nm (in water), essentially unchanged over the pH range 1–12. An earlier investigation with a 6-methoxyadenine nucleoside[19] had shown maximal absorption at 259 nm. This close correspondence of u.v. data, and the similarity in reaction conditions to those that had earlier produced the 9-*N*-linked product[19], support the conclusion that attachment of the sugar had occurred at N-9.

By a procedure analogous to that already described[1] for preparing isoxazole derivatives from protected, acetylenic sugar derivatives, the condensation of mesitylnitrile oxide with the L-*ido* acetylenic nucleoside analog **3** was effected. The reaction yielded a "double-headed nucleoside" analog **8**. This product was isolated by preparative t.l.c., and obtained pure as a white, amorphous material whose analysis indicated that it was a 1 : 1 adduct of the reactants. Its mass spectrum showed a small peak at highest mass-number for the molecular ion (*m/e* 631).

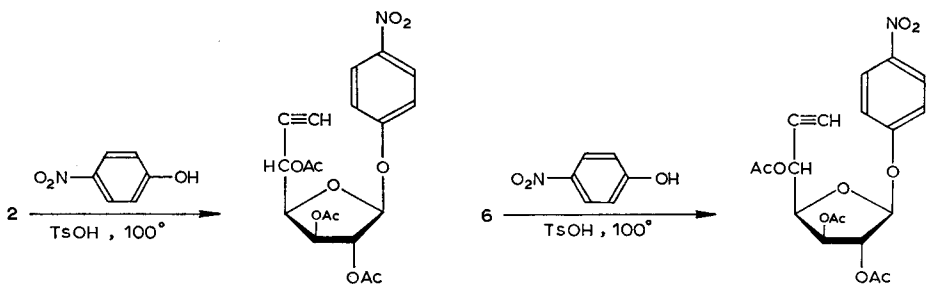


The ^{1}H-n.m.r. spectrum of **8** was straightforward, and only one set of resonances was observed, indicating a single regioisomer. The first-order spectrum observed was essentially a superposition of the separate ^{1}H-n.m.r. spectra of the L-*ido* acetylenic nucleoside **3** and the isoxazole derivative[1] from the L-*ido* acetylenic compound **1**. No signal for an acetylenic proton was observed; instead, a singlet at low field (δ 6.27) for the proton on the isoxazole ring was observed. The purine and mesityl ring-proton resonances were readily identified. The regioselectivity of the cycloaddition presumably follows that observed in the preceding work[1].

The D-*gluco* derivative **7** was treated with phenyl azide to give another type of "double-headed nucleoside" analog (**9**). The product was isolated by preparative t.l.c., and obtained crystalline in 62% yield.

The 100-MHz, ^{1}H-n.m.r. spectrum of **9** exhibited the patterns anticipated, considering the separate ^{1}H-n.m.r. spectra of the D-*gluco* acetylenic nucleoside **5** and the triazole derivative[1] obtained therefrom. The ^{1}H-n.m.r. spectra permitted the conclusion that the favored mode of cycloaddition is that already proposed[1,20] for reaction of phenyl azide with protected acetylenic sugars.

The fusion-reaction sequence of Helferich and Schmitz-Hillebrecht[21] was adapted for application to synthesis of aryl glycosides. The present synthesis was accomplished by a modification analogous to that of Lindberg and co-workers[22] for a phenyl glycoside. 1,2,3,5-Tetra-*O*-acetyl-6,7-dideoxy-α(and β)-L-*ido*-hept-6-ynofuranose (**2**) was fused with an excess of *p*-nitrophenol in the presence of *p*-toluenesulfonic acid at 100° to give a mixture of a major product and a minor proportion of unchanged starting-material. Purification of the acetylated glycoside **10** by preparative t.l.c. gave the glycoside **10** as a pale-yellow syrup in 39% yield. The D-*gluco* analog **11** was prepared in 44% yield from **6** by essentially the same procedure.



The i.r. spectra of both acetylated, *p*-nitrophenyl acetylenic glycosides showed absorptions at 3.05 and 4.68 μm, for the C–H and C≡C bonds of a terminal acetylenic group. The 100-MHz, ^{1}H-n.m.r. spectra of both isomers (**10** and **11**) showed the anticipated doublets for the acetylenic proton at δ 2.48 and 2.39, having spin-couplings of 2.0 Hz and 2.2 Hz for **10** and **11**, respectively. The H-1 resonances were observed as essential singlets (L-*ido*, δ 5.73; D-*gluco*, δ 5.72), indicating very small or zero coupling (<0.3 Hz) with H-2. The H-2 signals appeared as doublets showing a small spin-coupling with H-3 ($J_{2,3}$ for L-*ido*, 1.6 Hz; D-*gluco*, 1.7 Hz). The H-3 resonances were located as doublets of doublets showing the $J_{2,3}$ coupling and a second spacing, 5.5 Hz, the magnitude of which was taken as $J_{3,4}$. The H-4 and H-5 signals appeared as doublets of doublets.

The small magnitude of $J_{1,2}$ (<0.3 Hz) is consistent[23] with a *trans* relationship of H-1 and H-2, indicating the α-L (for **10**) and β-D (for **11**) configuration. Similar, small coupling-constants ($J_{1,2}$ ~2 Hz) have been observed[24] for the phenyl and *p*-nitrophenyl α-L-arabinofuranosides. The ^{1}H-n.m.r. spectra of several anomeric pairs

of methyl *O*-methyl-D-xylofuranosides have shown[25] $J_{1,2}$ values of 1.0 Hz for the β-D anomers, in contrast to a value for the α-D anomer of ~4.5 Hz.

There was no direct evidence for formation of the other furanosidic anomer, although, had it been present in traces, it might have escaped detection.

Thus, as already shown with respect to the nucleosides **3** and **7**, condensation of the acetylenic sugar derivatives **2** and **5** with *p*-nitrophenol also took place without disturbance to the acetylenic function or to the stereochemistry of the propargylic position.

EXPERIMENTAL

General methods. — Solutions were evaporated under diminished pressure (~15 mm) at 45°. Melting points were determined with a Thomas–Hoover "Unimelt" apparatus. T.l.c. was performed on Silica Gel G (E. Merck, Darmstadt, Germany) activated at 110°, with the developers *A*, 1:1 ether–petroleum ether (b.p. 30–60°); *B*, 3:1 chloroform–ether; *C*, 3:1 benzene–ether; or other solvents as indicated in parentheses. Unless otherwise specified, detection was effected by spraying the plates with 10% sulfuric acid and then heating. Column chromatography was performed with Silica Gel No. 7734 (0.05–0.2 mm mesh) (E. Merck AG, Darmstadt, W. Germany), with 1 g of the mixture to be separated per 30 g of adsorbent. Petroleum ether used was the fraction having b.p. 30–60°. Specific rotations were measured in a 1-dm tube with a Perkin–Elmer Model 141 photoelectric polarimeter. I.r. spectra were recorded with a Perkin–Elmer Model 137 spectrophotometer, and u.v. spectra with a Cary Model 14 spectrophotometer. ^{1}H-N.m.r. spectra were recorded at 100 MHz with a Varian HA-100 or a JEOL MH-100 spectrometer. Chemical shifts (δ) refer to an internal standard of tetramethylsilane (δ = 0). Elemental analyses were performed by W. N. Rond. X-Ray powder diffraction data give interplanar spacings, Å, for CuKα radiation. The camera diameter was 114.59 mm. Relative intensities were estimated visually: m, moderate; s, strong; v, very; w, weak. The strongest lines are numbered (1, strongest), and double numbers indicate approximately equal intensities. Mass spectra were recorded by C. R. Weisenberger with an AE1-MS-902 mass spectrometer at an ionizing potential of 70 eV, an accelerating potential of 8 kV, and a source temperature of 150°.

*1,2,3,5-Tetra-*O*-acetyl-6,7-dideoxy-*α(*and* β)-L-ido-*hept-6-ynofuranose* (**2**). — 3,5-Di-*O*-acetyl-6,7-dideoxy-1,2-*O*-isopropylidene-β-L-*ido*-hept-6-ynofuranose[3] (**1**, 880 mg) was deacetonated[12] by dissolving it in 9:1 (v/v) trifluoroacetic acid–water (10 mL). After dissolution, the solution was kept for 10 min at room temperature. The solvent was then evaporated off (bath temperature <50°) to give a solid residue. This product, without purification, was conventionally acetylated with acetic anhydride–sodium acetate, to give a syrupy peracetate **2**; yield 903 mg (89%). The crude, anomeric mixture of peracetates (**2**) thus obtained was used directly in condensation reactions with 2,6-dichloropurine and *p*-nitrophenol.

The ^{1}H-n.m.r. spectrum of the anomeric mixture in chloroform-*d* showed H-1

signals at δ 6.45 ($J_{1,2}$ 4.2 Hz) and 6.09 ($J_{1,2}$ <0.3 Hz) as doublets in the intensity ratio of 9:11.

*2,6-Dichloro-9-(2,3,5-tri-*O*-acetyl-6,7-dideoxy-*α*-*L*-ido-hept-6-ynofuranosyl)-9H-purine* (**3**). — A mixture of **2** (377 mg, 1.1 mmol), 2,6-dichloropurine (206 mg, 1.1 mmol), and *p*-toluenesulfonic acid (10 mg) was fused at 140° under diminished pressure until the vigorous evolution of acetic acid had ceased. Benzene (35 mL) was added to the mixture while it was still hot, and the solution was then allowed to cool. The benzene solution was washed with 5% aqueous sodium hydrogencarbonate (20 mL), dried (magnesium sulfate), and evaporated to a brown syrup. The product **3** was isolated by preparative t.l.c. on silica gel, with 3:1 benzene–ether as the eluant. Further purification by trituration in ether–petroleum ether gave **3** as a solid; yield 194 mg (37.4%); m.p. 96–98°, $[\alpha]_D^{25}$ +37.6° (*c* 0.5, chloroform); R_F 0.41 (*B*), 0.20 (*C*); λ_{max}^{KBr} 3.05 (C≡C-H), 4.68 (C≡C), 5.68 (C=O), 6.25, 6.40, and 6.68 μm (purine).

Anal. Calc. for $C_{18}H_{16}Cl_2N_4O_7$: C, 45.96; H, 3.40; Cl, 14.89; N, 11.92. Found: C, 45.85; H, 3.54; Cl, 15.10; N, 11.64.

*2-Chloro-9-(6,7-dideoxy-*α*-L-ido-hept-6-ynofuranosyl)-6-methoxy-9H-purine* (**4**). — Under anhydrous conditions, a solution of **3** (240 mg) in methanol (30 mL) was saturated at 0° with dry ammonia, and kept overnight at 0°. The solution was then evaporated, and the residue recrystallized from acetone–petroleum ether, to give **4** as needles; yield 120 mg (69%); m.p. 148–150°, $[\alpha]_D^{25}$ −31° (*c* 0.6, acetone); λ_{max}^{MeOH} 257 nm (ε_{mM} 13.0); $\lambda_{max}^{H_2O}$ 258 (ε_{mM} 9.76, pH 1), 257 (8.55, pH 7), and 257 nm (9.43, pH 12); R_F 0.73 (1:1 acetone–ether), 0.84 (1:1 chloroform–methanol); λ_{max}^{KBr} 2.90 (OH), 3.05 (C≡C-H), 4.70 (C≡C), 6.22, 6.30, and 6.78 μm (purine); X-ray powder diffraction pattern data: 8.19 vs (1), 5.71 s (2,2), 5.15 s (2,2), 4.15 m, 3.91 w, 3.71 m, 3.53 s (3), 3.39 vw, 3.12 w, and 2.89 m.

Anal. Calc. for $C_{13}H_{13}ClN_4O_5$: C, 45.88; H, 3.82; Cl, 10.29; N, 16.47. Found: C, 46.11; H, 3.78; Cl, 10.23; N, 16.20.

*1,2,3,5-Tetra-*O*-acetyl-6,7-dideoxy-*α*(and β)-D-gluco-hept-6-ynofuranose* (**6**). — Prepared from 3,5-di-*O*-acetyl-6,7-dideoxy-1,2-*O*-isopropylidene-α-D-*gluco*-hept-6-ynofuranose[3] (**5**, 900 mg) by the sequential deacetonation and acetylation previously described for the 5-epimer **1**, the reaction gave the peracetate **6** as a crude, syrupy, anomeric mixture; yield 940 mg. This syrup was used in the subsequent fusion-steps with 2,6-dichloropurine and *p*-nitrophenol.

The ^{1}H-n.m.r. spectrum of the anomeric mixture in chloroform-*d* showed H-1 signals at δ 6.47 ($J_{1,2}$ 4.4 Hz) and 6.16 ($J_{1,2}$ <0.3 Hz) as doublets, in the intensity ratio of 2:3.

*2,6-Dichloro-9-(2,3,5-tri-*O*-acetyl-6,7-dideoxy-β-D-gluco-hept-6-ynofuranosyl)-9H-purine* (**7**). — Prepared from crude **6** (621 mg), 2,6-dichloropurine (342 mg), and *p*-toluenesulfonic acid (10 mg) according to the method described for the *L-ido* analog **3**, compound **7** was obtained crystalline; yield 282 mg (33%); m.p. 169–170°, $[\alpha]_D^{25}$ +16.3° (*c* 0.6, chloroform); R_F 0.38 (*B*), 0.17 (*C*); λ_{max}^{KBr} 3.05 (C≡C-H), 4.68 (C≡C), 5.74 (C=O), 6.26, 6.42, and 6.68 μm (purine); X-ray powder diffraction

data: 11.78 vw, 10.16 s (2,2), 8.19 m (3,3,3), 7.31 w, 6.51 w, 6.10 w, 5.57 s (2,2), 4.41 m, 3.96 m, 3.80 w, 3.64 vs (1,1), 3.52 w, 3.40 vs (1,1), and 3.30 m (3,3,3).

Anal. Calc. for $C_{18}H_{16}Cl_2N_4O_7$: C, 45.96; H, 3.40; Cl, 14.89; N, 11.92. Found: C, 45.89; H, 3.60; Cl, 15.07; N, 11.77.

*2,6-Dichloro-9-[2,3,5-tri-*O*-acetyl-5-*C*-(3-mesitylisoxazol-5-yl)-α-*L*-ido-pentofuranosyl]-9H-purine* (**8**). — A solution of **3** (220 mg, 0.47 mmol) and 2,4,6-trimethylbenzonitrile *N*-oxide (77 mg, 0.48 mmol) in benzene (15 mL) was boiled gently for 15 min under reflux, and then evaporated. The solid product was purified by preparative t.l.c. on silica gel, with 2:1 benzene–ether as the eluant. Further purification by trituration with ether–petroleum ether gave pure, amorphous **8**; yield 192 mg (65%), m.p. 110–112°, $[\alpha]_D^{25}$ +37.5° (*c* 0.5, chloroform); λ_{max}^{MeOH} 274 (ε_{mM} 10.3), 248 (9.60), and 209 nm (41.1); R_F 0.53 (ether), 0.30 (*B*); λ_{max}^{KBr} 3.40 (Ar), 5.68 (C=O), 6.25, 6.40, and 6.70 μm (purine and C=C of heterocycle).

Anal. Calc. for $C_{28}H_{27}Cl_2N_5O_8$: C, 53.24; H, 4.27; Cl, 11.09; N, 11.09. Found: C, 53.44; H, 4.49; Cl, 11.38; N, 10.87.

This product, although obtained as a solid, did not give an X-ray diffractogram indicative of a crystalline compound.

*2,6-Dichloro-9-[2,3,5-tri-*O*-acetyl-5-*C*-(1-phenyl-1,2,3-triazol-4-yl)-β-*D*-gluco-pentofuranosyl]-9H-purine* (**9**). — The *D-gluco* acetylenic nucleoside derivative **7** (265 mg, 0.56 mmol) was treated with phenyl azide (1 mL, 9.31 mmol) in the same way as in previous work[20]. The excess of reagent was removed under diminished pressure, and the brown residue was chromatographed by preparative t.l.c. on silica gel, with 2:1 benzene–ether as the eluant, to give **9**. Further trituration with ether–petroleum ether gave pure **9**; yield 207 mg (62%), m.p. 128–130°, $[\alpha]_D^{25}$ +2.8° (*c* 0.6, chloroform); λ_{max}^{MeOH} 268 (ε_{mM} 10.6) and 245 nm (13.2); R_F 0.53 (ether), 0.36 (*B*); λ_{max}^{KBr} 3.40 (Ar), 5.70 (C=O), 6.25, 6.40, and 6.68 μm (aryl C=C); X-ray powder diffraction data: 12.45 vs (1), 10.40 m, 9.71 m, 8.11 w, 7.19 vw, 6.65 s (2), and 6.32 (w).

Anal. Calc. for $C_{24}H_{21}Cl_2N_7O_7$: C, 48.89; H, 3.67; Cl, 11.88; N, 16.63. Found: C, 49.11; H, 3.92; Cl, 12.08; N, 16.75.

p-*Nitrophenyl 2,3,5-tri-*O*-acetyl-6,7-dideoxy-α-*L*-ido-hept-6-ynofuranoside* (**10**). — *p*-Nitrophenol (453 mg), *p*-toluenesulfonic acid (10 mg), and compound **2** (400 mg, 1.17 mmol) were melted together, and heated for 30 min at 100° (water-aspirator pressure), to give a dark-brown mixture. Benzene (30 mL) was added to the mixture while still hot, and the solution was successively washed with water and 5% aqueous sodium hydrogencarbonate (20 mL), dried (magnesium sulfate), and evaporated to a syrup. Purification of the acetylated glycoside by preparative t.l.c. with 1:1 ether–petroleum ether as the eluant gave **10** as a pale-yellow syrup; yield 193 mg (39.2%), $[\alpha]_D^{25}$ −113° (*c* 1.0, chloroform); R_F 0.47 (*A*), 0.77 (*B*); λ_{max}^{film} 3.05 (C≡C-H), 3.34 (Ar-H), 4.68 (C≡C), 5.68 (C=O), 6.18, 6.22 (Ar), 6.58, 6.68, 7.28, 7.42 (NO_2), 8.20 (C-O), and 13.28 μm (aryl).

Anal. Calc. for $C_{19}H_{15}NO_{10}$: C, 54.15; H, 4.51; N, 3.32. Found: C, 54.32; H, 4.67; N, 3.31.

p-*Nitrophenyl 2,3,5-tri-*O*-acetyl-6,7-dideoxy-β-*D*-gluco-hept-6-ynofuranoside*

(**11**). — A mixture of compound **6** (370 mg, 1.08 mmol), *p*-nitrophenol (453 mg), and *p*-toluenesulfonic acid (10 mg) was treated in the same way as described for synthesis of the L-*ido* analog **10**. Purification by preparative t.l.c., with 1:1 ether–petroleum ether as the eluant, gave **6** as a syrup; yield 203 mg (44.6%), $[\alpha]_D^{25}$ +14.2° (*c* 0.8, chloroform); R_F 0.50 (*A*), 0.77 (*B*); λ_{max}^{film} 3.05 (C≡C-H), 3.35 (Ar-H), 4.68 (C≡C), 5.70 (C=O), 6.20, 6.26 (Ar), 6.60, 6.70, 7.30, 7.45 (NO_2), 8.15 (C-O), and 13.30 μm (aryl).

Anal. Calc. for $C_{19}H_{15}NO_{10}$: C, 54.15; H, 4.51; N, 3.32. Found: C, 54.45; H, 4.63; N, 3.45.

ACKNOWLEDGMENT

The authors thank Dr. S. J. Eitelman for recording the n.m.r. spectra.

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