of red phosphorus at 150° for 1 hr. The reaction mixture was cooled, neutralized with concentrated ammonium hydroxide, and centrifuged. The supernatant, containing **9**, was chromatographed on Whatman No. 1 paper (ammonia–water solvent (pH 10.0)). The ultraviolet spot corresponding to the chemically synthesized 4-hydroxypyrrolo[2,3-*d*]pyrimidine was cut out and eluted with water. The yield was 1.5 μmoles (40%). The R_f and the ultraviolet spectra of the 4-hydroxypyrrolo-[2,3-*d*]pyrimidine were identical with those of the chemically synthesized compound supplied by Dr. G. H. Hitchings and reported by Ohkuma:[5] $\lambda_{max}^{0.1\,N\,HCl}$ 263 mμ; $\lambda_{max}^{0.1\,N\,NaOH}$ 265 mμ.

The isolation of 4-hydroxypyrrolo[2,3-*d*]pyrimidine (**9**) from tubercidin was accomplished by treatment of the nucleoside with nitrous acid[12] followed by a 5-hr reflux with 1 *N* HCl.[7] The reaction mixture was cooled to room temperature and barium carbonate was added to neutralize the sulfuric acid. The barium sulfate was removed by filtration. The aqueous fraction was evaporated to a small volume, applied to a Whatman No. 1 paper chromatogram, and developed in 1-butanol–1 *N* NH_4OH (86:14). The R_f value of the 4-hydroxypyrrolo-[2,3-*d*]pyrimidine (**9**), detected by ultraviolet light, was identical with that of authentic compound. The area was cut out and eluted with water. The ultraviolet spectra was the same as that reported for the synthetic compound.

4-Aminopyrrolo[2,3-*d*]pyrimidine (10) (from Tubercidin).—Tubercidin (**1**) (150 μmoles) was oxidized with periodate in exactly the same manner as described above for the oxidation of toyocamycin. The aglycon **10** was crystallized from water. The yield was 31 μmoles (21%). There was one ultraviolet spot as determined by a thin layer of chromatography. The infrared spectra of the isolated and chemically synthesized 4-aminopyrrolo[2,3-*d*]pyrimidine were the same (3400 and 3100 cm^{-1} (NH), 1650 and 1600 cm^{-1} (C=N)). The ultraviolet spectra was the same as that reported above for the synthesized compound.

Registry No.—**1**, 69-33-0; **3**, 1414-35-3; **5**, 1500-90-9; **6**, 1534-21-0; **8**, 15023-88-8; **9**, 3680-71-5; **10**, 1500-85-2.

(12) J. E. Pike, L. Slechta, and P. F. Wiley, *J. Heterocyclic Chem.*, **1**, 159 (1964).

Extension of Sugar Chains through Acetylenic Intermediates. IV. Derivatives of 1-Pentyne-D-*erythro*(and D-*threo*)-3,4,5-triol[1-3]

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Received July 7, 1967

Ethynylation of 2,3-*O*-isopropylidene-*aldehydo*-D-glyceraldehyde (**1**) gives a 44:56 mixture of 4,5-*O*-isopropylidene-1-pentyne-D-*erythro*(and D-*threo*)-3,4,5-triol (**2** and **7**), separable by glpc as their 3-acetates **3** and **8**. Hemihydrogenation of **3** and **8** gave the derived pentenes **4** and **9**, also obtainable, in admixture, by vinylation of **1** and acetylation of the product. The epimers were individually identified by degradation; the acetates **3** and **8** were ozonized and the products were hydrolyzed to give an erythronolactone and a threonolactone, respectively, and the pentenes **4** and **9** were successively ozonized, reduced, and hydrolyzed to give erythritol and a threitol, respectively. Saponification of **3** and **8** gave the separate epimers **2** and **7**, which were converted into their crystalline 3-(3,5-dinitrobenzoates) **17** and **18**. The esters (**3** and **17**) having the D-*erythro* configuration showed spin–spin couplings between H-3 and H-4 smaller than those of the D-*threo* analogs (**8** and **18**), indicating that the most populated rotamer state of these acetylenic derivatives is that having the 3-acyloxy group antiparallel, and the ethynyl group *gauche*, to the C-5 carbon atom.

In an earlier paper[4] in this series, the ethynylation of 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-L-arabinose to give the 4,5:6,7-diisopropylidene acetal of 1-heptyne-L-*gluco*(and L-*manno*)-pentol was described. The epimers were separated by glpc, and also by fractional crystallization of suitable derivatives, and their structures were proved by two independent degradative routes. It was shown that the epimers could be differentiated readily by nmr spectroscopy of various 3-*O*-acyl derivatives; the coupling of H-3 with H-4 was correlated with the relative configuration at C-3 and C-4. In the present report, the ethynylation of 2,3-*O*-isopropylidene-*aldehydo*-D-glyceraldehyde (**1**) to give a mixture of 4,5-*O*-isopropylidene-1-pentyne-D-*erythro*-3,4,5-triol[5] (**2**) and 4,5-*O*-isopropylidene-1-pentyne-D-*threo*-3,4,5-triol[5] (**7**) is described, together with the separation of the epimers, structural proofs by degradative methods, and characterization of the acetylenic compounds and their derived alkenes by nmr spectroscopy and mass spectroscopy.

2,3-*O*-Isopropylidene-*aldehydo*-D-glyceraldehyde (**1**) was prepared by oxidation of 1,2:5,6-di-*O*-isopropylidene-D-mannitol[6] with lead tetraacetate by the procedure of Baer and Fischer,[7] and azeotropic coevaporation of the crude product with carbon tetrachloride was employed to remove all acetic acid before vacuum distillation of the product. Omission of this step gave **1** containing some acetic acid, detected by nmr spectroscopy, which could not readily be removed by distillation and which led to diminution of yield in the ethynylation step. The nmr spectrum of the freshly prepared aldehyde **1** showed the anticipated low-field signal for the aldehyde proton at τ 0.35 as a one-proton, narrow doublet, $J_{1,2}$ = 1.7 Hz. On storage at room temperature, substance **1** polymerized,[7] as manifested in observed changes in the nmr and ir spectra of the material.

(1) Previous paper in this series: J. L. Godman, D. Horton, and J. M. J. Tronchet, *Carbohydrate Res.*, **4**, 392 (1967).

(2) Preliminary reports of this work have been given: (a) D. Horton, J. B. Hughes, and J. M. J. Tronchet, *Chem. Commun.*, 481 (1965); (b) D. Horton, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 21D; (c) presented at the 4th Gordon Research Conference on Carbohydrates, Tilton, N. H., July 1966.

(3) Supported by the National Institutes of Health, Public Health Service, Department of Health, Education, and Welfare, Bethesda, Md. 20014; Grant No. GM-11976-02 (The Ohio State University Research Foundation Project 1820). Funds for the nmr spectrometer were provided by the National Science Foundation, Washington, D. C.

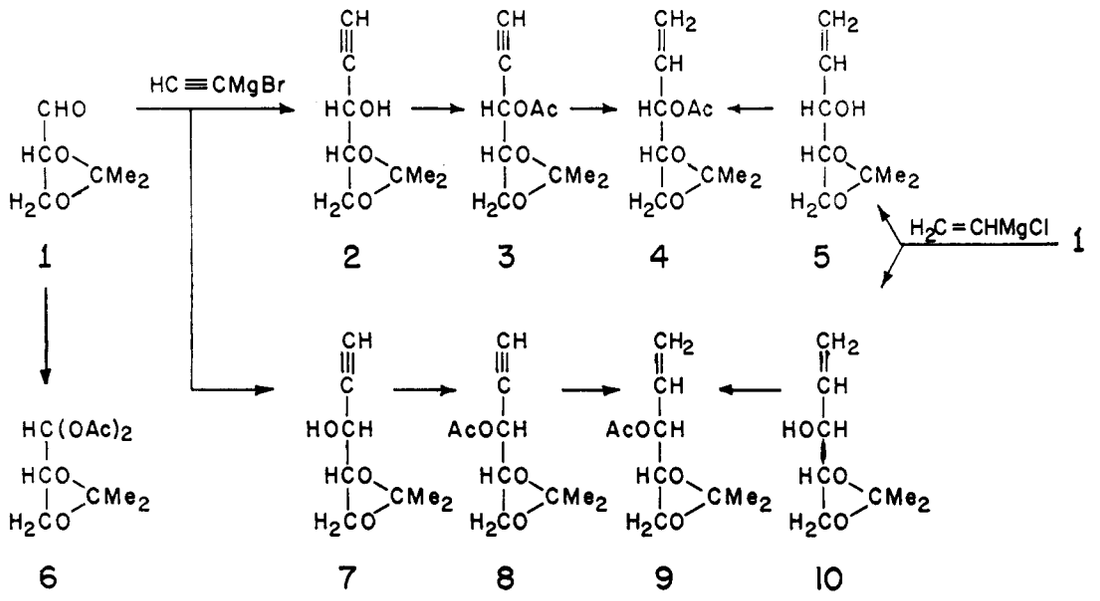
(4) D. Horton and J. M. J. Tronchet, *Carbohydrate Res.*, **2**, 315 (1966).

(5) Compounds **2** and **7** are strictly named as 1,2-*O*-isopropylidene-4-pentyne-L-*erythro*- and -D-*threo*-1,2,3-triol, respectively. In this paper, as in preceding ones,[1,4] the alkyne terminus is considered to be C-1, so that configurational relationships are readily apparent between the acetylenic derivatives, their precursors, and their degradation products.

(6) H. O. L. Fischer and G. Dangschat, *Ber.*, **65**, 1038 (1932).

(7) E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **128**, 463 (1939).

SCHEME I



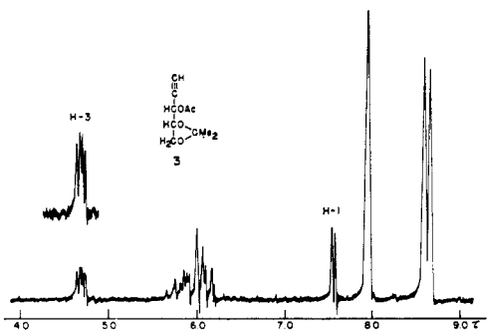


Figure 1.—The 60-MHz nmr spectrum of 3-*O*-acetyl-4,5-*O*-isopropylidene-1-pentyne-D-*erythro*-3,4,5-triol (**3**) in chloroform-*d*.

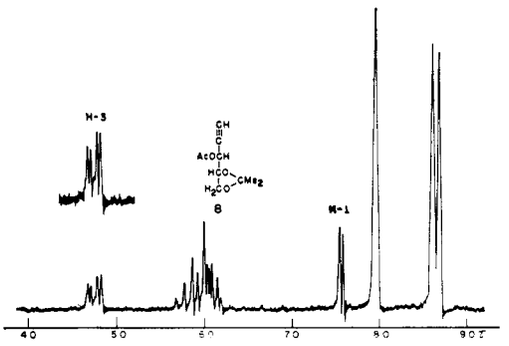


Figure 2.—The 60-MHz nmr spectrum of 3-*O*-acetyl-4,5-*O*-isopropylidene-1-pentyne-D-*threo*-3,4,5-triol (**8**) in chloroform-*d*.

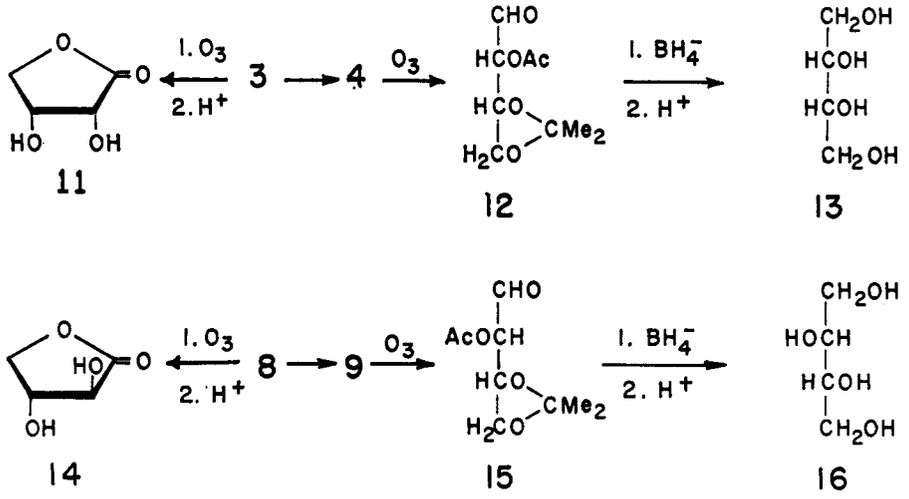
Ethynylation of the freshly prepared aldehyde **1** with an excess of ethynylmagnesium bromide (see Scheme I) gave the mixed, epimeric acetylenic alcohols **2** and **7** as a liquid, in almost quantitative yield. This epimeric mixture migrated on tlc as a single zone, and its nmr spectrum provided firm support for the structures (**2** and **7**) assigned. Integration of the signals for the acetylenic proton (H-1), the *gem*-dimethyl group, the hydroxyl hydrogen atom, and the H-3,4,5, and 5′ groups, gave the anticipated 1:6:1:4 ratio, and the signal assigned to the proton of the hydroxyl group was exchangeable by deuteration; the acetylenic proton was not detectably exchanged by deuterium oxide in chloroform-*d*. The fact that the H-1 signal had a relative intensity of one proton indicated that little if any 1,2-disubstituted acetylene was present, and the absence of observed signals below τ 5.5 indicated that little if any unreacted aldehyde **1** remained. The signal of the acetylenic proton, observed in chloroform-*d* near τ 7.5, was observed 0.4 ppm to lower field in deuterium oxide. The signals for H-3,4,5, and 5′ gave a complex multiplet, not amenable to simple analysis. The mixture of **2** and **7** could be distilled, but no separation of the epimers could be achieved. The two compounds were likewise unresolved in several glpc and tlc systems examined.

Acetylation of the mixture of **2** and **7** gave the corresponding mixture of 3-acetates (**3** and **8**) as a liquid, in essentially quantitative yield. Integrated nmr spectra again provided reliable indication of the structure and purity of the product, with signals in a 1:3:1:3:6 relationship, assigned to H-3, the H-4,5,5′ group, H-1, the acetyl group, and the *O*-isopropylidene group, respectively. A minor, high-boiling side-product that was formed in some preparations of **2** and **7** appeared, from its nmr spectrum, to be the acetylated aldehydrol **6** of the starting aldehyde **1** (Scheme I). A second side-product, having a low boiling point, was also detected. The side products usually amounted to <5% of the total product.

Separation of the epimeric 3-acetates **3** and **8** was not achieved by tlc, but preparative glpc on a poly(ethylene glycol) (Carbowax) column permitted effective separation of the two compounds in complete epimeric purity. The nmr spectra of the separated products are shown in Figures 1 and 2. In common with other propargyl alcohol derivatives,[1,2a,4] the acetylenic proton shows a small (~2 Hz) coupling with the proton four bonds distant ($J_{1,3}$). The only significant difference between the spectra of the epimers is the spin coupling between H-3 and H-4, which can be measured from the spacings of the H-3 signal, and which is considerably larger in one epimer than in the other.

Hemihydrogenation of the acetylenic derivatives **3** and **8**, singly or in admixture, was effected smoothly over a partially poisoned palladium catalyst (Lindlar

SCHEME II



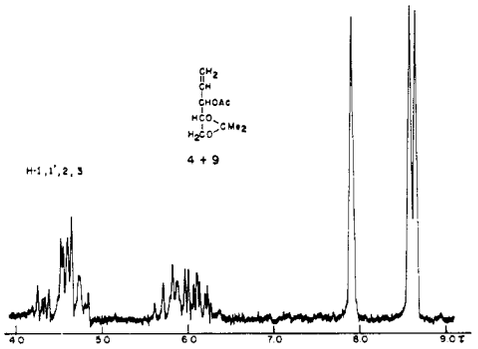


Figure 3.—The 60-MHz spectrum of 3-*O*-acetyl-4,5-*O*-isopropylidene-1-pentene-D-*erythro*(and D-*threo*)-3,4,5-triol (**4** and **9**) as a neat liquid.

catalyst),[8] and nmr spectroscopy provided a very sensitive index of the extent of reduction.[4] The reduction was terminated without difficulty at the alkene stage, and the nmr spectrum (Figure 3) of the mixture of alkenes (**4** and **9**) obtained from the mixed acetylenes **3** and **8** clearly shows absence of the acetylenic proton signal, and presence of a four-proton multiplet at low field, assigned to the three vinylic hydrogen atoms, and the more highly deshielded methine hydrogen atom (H-3). Over-reduction was readily detected by the diminution in intensity of the low-field signals, and the appearance of signals characteristic of an ethyl group.

Mass spectrometry of the alkynes **3** and **8**, and the alkenes **4** and **9**, revealed no appreciable peak corresponding to the molecular ion, but in each case a substantial peak corresponding to the M − 15 ion (*m/e* 183 for **3** and **8**, *m/e* 185 for **4** and **9**) was observed. This observation is in agreement with the reported behavior of other isopropylidene acetals, which typically lose one methyl group to give the largest observed fragment.[9,10] A further listing of fragmentation products is given in the Experimental Section.

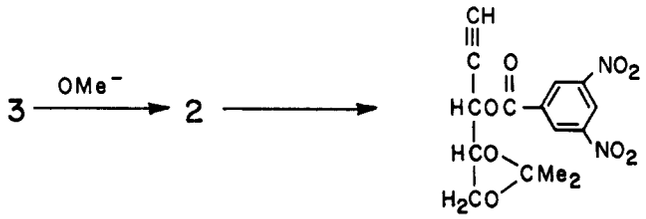
The mixture of alkenes **4** and **9** could also be obtained by vinylation of the aldehyde **1** to give a mixture of allylic alcohols **5** and **10**, followed by acetylation to give **4** and **9**. This route to the alkenes was of limited value, because a chromatographic method for separating **4** and **9** was not found.

The configurations of the two epimeric series of 5-carbon compounds were established by two independent routes, following methods developed in an earlier paper.[4] Each route sets out from the acetylenic 3-acetates **3** and **8** (see Scheme II). The epimer having the shorter retention time ($[\alpha]^{20}D$ −52.8° in chloroform), which formed 56% of the epimeric mixture, was ozonized to cleave the triple bond and convert C-2 into a carboxyl group. This acid was hydrolyzed, and the product was found to be indistinguishable by chromatography from D(or L)-threonolactone but different from D(or L)-erythronolactone; the product must, therefore be D-threonolactone (**14**). The levorotatory acetylene derivative was identified, therefore, as the D-*threo* isomer **8**. The epimer having the longer retention time ($[\alpha]D$ +71.4° in chloroform), which formed 44% of the epimeric mixture, was similarly degraded by ozonolysis and hydrolysis, to give a product identified as D-erythronolactone (**11**), thus establishing the dextrorotatory acetylene derivative as the D-*erythro* isomer **8**. The second proof sets out from the derived alkenes **4** and **9**, which were ozonized to the *aldehydo*-tetrose derivatives **12** and **15**, reduced with borohydride to the substituted tetritols, and then hydrolyzed, to give erythritol (**13**) and a threitol (D-threitol, **16**), respectively. They were identified by their characteristically different migration rates on paper electrophoresis in a molybdate buffer[11] and as their crystalline tetrakis(*p*-nitrobenzoates).

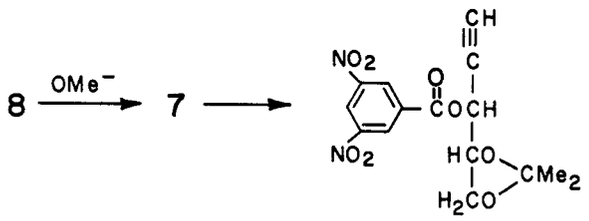
The individual acetylenic alcohols **2** and **7** could not be obtained by separation of the mixture produced by ethynylation of the aldehyde **1**, but they were readily prepared by saponification of the separated acetates **3** and **8** (Scheme III). The alcohols **2** and **7** gave stable, crystalline 3-(3,5-dinitrobenzoates) (**17** and **18**, respectively). The D-*erythro* isomer (**17**) had mp 133° and $[\alpha]D$ +50° (in chloroform), and the D-*threo* isomer (**18**) had mp 134° and $[\alpha]D$ −31.5° (in chloroform); in admixture the melting point was depressed by over 40°.

(8) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).
(9) D. C. DeJongh and K. Biemann, *J. Am. Chem. Soc.*, **86**, 67 (1964).
(10) N. K. Kochetkov and O. S. Chizhov, *Advan. Carbohydrate Chem.*, **21**, 39 (1966).
(11) E. J. Bourne, D. H. Hutson, and H. Weigel, *J. Chem. Soc.*, 35 (1961).

SCHEME III

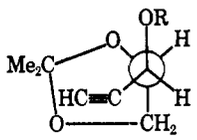


17

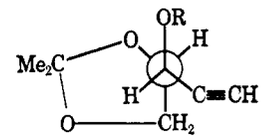


18

In the two epimeric pairs of 3-*O*-acyl derivatives, **3** and **8** and **17** and **18**, it was possible to observe the H-3 signal in the nmr spectrum (Figures 1 and 2) as a well-resolved quartet, whose spacings were those of the $J_{1,3}$ first-order coupling (also observed in the H-1 signal) and the $J_{3,4}$ coupling. The *erythro* isomers each gave a narrow quartet for H-3 ($J_{3,4}$ = 3.8 Hz for **3**, 3.8 Hz for **17**), and the *threo* isomers gave a wider quartet ($J_{3,4}$ = 6.8 Hz for **8** and 7.3 Hz for **17**). This is in accord with previous observations on seven-carbon analogs[4] and indicates that the most highly populated rotamer state in each derivative is that in which the 3-acyloxy group is antiparallel to C-5, as shown in Newman projection formulas. It is known from



erythro
3, R = Ac; $J_{3,4}$ = 3.8 Hz
17, R = 3,5-dinitrobenzoyl; $J_{3,4}$ = 3.8 Hz



threo
8, R = Ac; $J_{3,4}$ = 6.8 Hz
18, R = 3,5-dinitrobenzoyl; $J_{3,4}$ = 7.1 Hz

studies in cyclohexane systems[12] that the stereoelectronic requirements of an OR group exceed those of the ethynyl group. The results of present and previous[4] work indicated that it may be possible to assign configuration at C-3 in ethynylated derivatives of aldehydo sugars by observing the relative magnitudes of the $J_{3,4}$ values for an epimeric pair of 3-*O*-acyl derivatives.

The ease of preparation of the ethynylated sugars, the fact that the epimers can be separated and their structures assigned and the great synthetic versatility of the acetylene group, suggests that acetylenic sugar derivatives may find wide utility in sugar synthesis. The present paper and earlier reports[1,2,4] describe high-yielding sequences that constitute one-carbon, chain-extension reactions to higher aldoses and aldonic acids, and it has been shown[4] that the acetylenic alcohol system is stable under the conditions normally employed for acid hydrolysis of glycosides and acetals and *O*-deacylation conditions. Forthcoming reports will be concerned with conversions of the acetylenic sugar derivatives into α,β-unsaturated aldehydes,[2a] synthesis of branched-chain structures[13] by ethynylation of keto sugar derivatives,[14] and other reactions of acetylenic sugar derivatives.

(12) R. J. Ouellette, *J. Am. Chem. Soc.*, **86**, 3089 (1964).

Experimental Section[15]

Preparation of 2,3-*O*-Isopropylidene-*aldehydo*-D-glyceraldehyde (1).—The general procedure of Baer and Fischer[7] was followed. To a solution of 1,2:5,6-di-*O*-isopropylidene-D-mannitol[6] (50 g) in dry benzene (500 ml) was added ~90 g of fresh lead tetraacetate,[16] slowly with stirring. After 3.0 hr the mixture was filtered, and the filtrate was concentrated below 25° to a syrup, from which four 30-ml quantities of carbon tetrachloride were evaporated. The vacuum of a water aspirator was used, and the temperature was maintained below 25°. The syrup was then distilled in a vacuum. The first few milliliters of product were discarded, and the main fraction of **1** was collected, yield 34.0 g (68%): bp 31° (5 torr) (lit.[7] bp 35–42° (8–11 torr)); λ_{max}^{film} 3.58 (CHO), 5.75 (C=O), 7.25, 7.30 μm (CMe_2); nmr (neat), τ 0.35 (one-proton doublet, $J_{1,2}$ = 1.7 Hz, H-1), 5.60 (one-proton sextet, width = 13 Hz, H-2), 5.75–6.05 (two-proton multiplet, H-3,3'), 8.56, 8.61 (three-proton singlets, CMe_2).

Higher yields of distilled product could be obtained if the step of coevaporation with carbon tetrachloride was omitted, but the nmr spectrum of the product revealed the presence of acetic acid, which could not be removed entirely, even by repeated fractional distillation.

The product was unstable on storage, and changes were observed in the ir and nmr spectra of a sample of **1** that had been kept at room temperature for several days; the signal for the aldehyde proton in the nmr spectrum diminished in intensity.

4,5-*O*-Isopropylidene-1-pentyne-D-*erythro*(and D-*threo*)-3,4,5-triol (2 and 7).—A solution of ethylmagnesium bromide, prepared from magnesium (6.0 g) and ethyl bromide (42 g, 30 ml) in dry tetrahydrofuran (400 ml), was added dropwise to tetrahydrofuran (700 ml) through which a stream of acetylene was passed before, during, and after the addition. To the resultant pink solution a solution of freshly distilled 2,3-*O*-isopropylidene-*aldehydo*-D-glyceraldehyde (**1**, 28.3 g) in tetrahydrofuran (50 ml) was added dropwise with stirring at room temperature. A slow stream of acetylene was passed through the solution throughout the reaction period. The solution was stirred for a further 2 hr, concentrated to 500 ml, and washed at 0° three times with 100-ml portions of saturated aqueous ammonium chloride. The aqueous washings were extracted twice with 100-ml portions of ether, and the combined organic phases were dried (magnesium sulfate) and evaporated to give the mixed epimers **2** and **7** as a colorless syrup, yield 36.8 g (quantitative), and homogeneous by tlc, R_f 0.6 (1:19 methanol–benzene):

(13) A. K. Chatterjee, A. E. El-Ashmawy, D. Horton, J. S. Jewell, L. G. Magbanua, W. E. Mast, K. D. Philips, and J. D. Wander, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p D19.

(14) D. Horton and J. S. Jewell, *Carbohydrate Res.*, **5**, 149 (1967).

(15) Melting points were determined with a Thomas–Hoover "Unimelt" apparatus (Arthur H. Thomas Co., Philadelphia, Pa.). Optical rotations were determined in a 2-dm polarimeter tube. Infrared spectra were measured with a Perkin-Elmer Model 137 infrared spectrophotometer. Nuclear magnetic resonance spectra were measured with a Varian A-60 nmr spectrometer, with tetramethylsilane (τ = 10.00) as the internal standard for solutions in chloroform-*d* or neat liquids and sodium 4,4-dimethyl-4-silapentane-1-sulfonate as internal standard for solutions in deuterium oxide. Spectral analyses are first order and the recorded *J* values are the measured line spacings, measured with an accuracy of ±0.3 Hz or better. Mass spectra were measured with an AEI Model MS-9 high-resolution mass spectrometer; data give *m/e* values of peaks, and their per cent intensities relative to one of the principal peaks. Microanalyses were determined by W. N. Rond. X-Ray powder diffraction data give interplanar spacings, *A*, for Cu Kα radiation. The camera diameter was 114.59 mm. Relative intensities were estimated visually: s, strong; m, moderate; w, weak; v, very. The strongest lines are numbered in order (1, strongest). Thin-layer chromatography was performed with silica gel G, activated for 2 hr at 110°, as the adsorbent and indication was effected with sulfuric acid.

(16) G. Frederick Smith Co., Columbus, Ohio.

λ_{max}^{film} 2.95 (OH), 3.10 (C≡H), 4.75 (C≡C), 7.28 μm (CMe_2); nmr (chloroform-*d*), τ 5.50–6.20 (four-proton multiplet, H-3,4, 5,5′), 6.54 (one-proton broadened singlet, disappears on deuteration, OH), 7.49 (one-proton broadened doublet, $J_{1,3}$ = ~1.7 Hz, H-1), 8.54, 8.62 (three-proton singlets, CMe_2); nmr (deuterium oxide), τ 5.55–6.20 (four-proton multiplet, H-3,4,5,5′), 7.11 (one-proton doublet, $J_{1,3}$ = ~2 Hz, H-1), 8.55, 8.64 (CMe_2). The product was distilled at 59–60° (0.15–0.20 torr).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.51; H, 7.75. Found: C, 61.49; H, 7.74.

The chemical shift of the H-1 signal (in chloroform-*d*) varied slightly with concentration. No signals between τ −2.0 and 5.5 were observed in the crude reaction product. The product was eluted as a single peak from a glpc column of Carbowax 20M, under conditions wherein good separation of the derived 3-acetates (**3** and **8**) was obtained.

3-*O*-Acetyl-4,5-*O*-isopropylidene-1-pentyne-D-*erythro*(and D-*threo*)-3,4,5-triol (3 and 8).—The syrup (**2** and **7**) from the preceding preparation (33 g) was dissolved in acetic anhydride (180 ml), anhydrous sodium acetate (17 g) was added, the mixture was heated for 30 min at 95° and then 1 min at its boiling point, and the cooled solution was poured into ice and water (1000 ml). After 1 hr, the solution was extracted with three 100-ml portions of dichloromethane, the extract was washed with water (200 ml) and saturated aqueous sodium hydrogen carbonate (200 ml), and the dried (magnesium sulfate) extract was evaporated to a colorless syrupy mixture of **3** and **8**, yield 41.5 g (quantitative), which was distilled at 51° (0.02 torr).[17] The product had R_f 0.73 (9:1 chloroform–ether); λ_{max}^{film} 3.09 (C≡CH), 4.71 (C≡C), 5.70, 5.75 (OAc), 7.25, 7.30 μm (CMe_2); nmr (neat), τ 6.50–6.70 (one-proton multiplet, H-3), 5.50–6.25 (three-proton multiplet, H-4,5,5′), 7.25 (one-proton narrow quartet, H-1), 7.96 (three-proton singlet, OAc), 8.64, 8.70 (three-proton singlets, CMe_2).

In some preparations, a small (<5%) amount of a side-product having R_f 0.9 (9:1 chloroform–ether) was detected, and was isolated from a residual fraction that boiled at ~20° higher than the principal product. The nmr spectrum of this product in chloroform showed τ 3.20 (one-proton doublet, $J_{1,2}$ = 4.7 Hz, H-1), 5.50–6.13 (three-proton multiplet, H-2,3,3′), 7.93 (six-proton singlet, OAc), 8.59, 8.65 (three-proton singlets, CMe_2), suggesting that it was the acetylated aldehydrol (**6**) of **1**. This side-product could be detected in the crude mixture of **3** and **8** by the appearance of the doublet at τ 3.20 in the nmr spectrum. Very little of this side-product was formed when precautions were taken to ensure complete ethynylation of **1** before the acetylation step.

Separation of the 3-Acetates 3 and 8.—The mixture of **3** and **8** was resolved by preparative glpc on a 20 ft × 3/8 in. stainless-steel column packed with 30% Carbowax[18] 20M on 60–80 mesh, acid-washed Chromosorb[18] W. An Aerograph Autoprep, Model 705, gas chromatograph,[19] equipped for automatic injection of samples and collection of fractions, was used. Nitrogen, at an inlet pressure of 65 psi, was used as the carrier gas, at a flow rate of 200 cc/min, and the column temperature was maintained at 200–205°. The effluent stream passed through a 1:10 stream splitter, and the minor stream passed to a flame-ionization detector. A 10% solution of the mixture of **3** and **8** in methanol was injected in 0.2-ml portions, and the collection bottles of the fraction collector connected to the major effluent stream were cooled to −80°. Principal components having retention times of 50 and 56 min were observed as two separate peaks of >80% resolution. Integration of the recorder response indicated that the two components were present in 56:44 proportion. A minor side-product, approximately 3% of the two main products, was eluted after 26 min. The major products were collected, and their purity was checked by reinjection into the chromatograph; the collected samples of each component contained 0–5% of the other component. Samples were rechromatographed, where necessary, until each component contained no detectable proportion of the other.

The faster moving, principal product, with a retention time of 50 min and a relative yield of 56%, was identified as **3-*O*-acetyl-4,5-*O*-isopropylidene-1-pentyne-D-*threo*-3,4,5-triol (8)**: $[\alpha]^{20}D$ −52.8 ± 0.2° (*c* 5.1, chloroform); λ_{max}^{film} 3.05 (C≡CH), 4.71 (C≡C), 5.72 (OAc), 7.28 μm (CMe_2); nmr (chloroform-*d*, see Figure 1), τ 4.60 (one-proton quartet, $J_{1,3}$ = 2.2 Hz, $J_{3,4}$ = 6.8 Hz, H-3), 5.55–6.08 (three-proton multiplet, H-4,5,5′), 7.52 (one-proton doublet, H-1), 7.89 (three-proton singlet, OAc), 8.56, 8.64 (three-proton singlets, CMe_2).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.00; H, 7.45.

The slower moving, principal product, retention time 56 min, relative yield 44%, was identified as **3-*O*-acetyl-4,5-*O*-isopropylidene-1-pentyne-D-*erythro*-3,4,5-triol (3)**: $[\alpha]^{19}D$ +71.4 ± 0.2° (*c* 4.4, chloroform); λ_{max}^{film} 3.05 (C≡CH), 4.69 (C≡C), 5.72 (OAc), 7.28 μm (CMe_2); nmr (chloroform-*d*, see Figure 2), τ 4.57 (one-proton quartet, $J_{1,3}$ = 2.2 Hz, $J_{3,4}$ = 3.8 Hz, H-3), 5.53–6.07 (three-proton multiplet, H-4,5,5′), 7.48 (one-proton doublet, H-1), 7.88 (three-proton singlet, OAc), 8.57, 8.65 (three-proton singlets, CMe_2).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.52; H, 7.09.

The ir spectra of **3** and **8** were very similar between 2.5 and 8 μm, but showed small differences at longer wavelength; **8** showed peaks at 8.2 s, 8.72 m, 9.35 s, 9.75 s, 10.35 m, 11.0 w, 11.33 w, 11.89 s, and 12.7 w μm; and **3** showed peaks at 8.2 s, 8.68 m, 8.91 w, 9.38 s, 9.85 s, 10.15 w, 10.38 w, 11.00 m, 11.88 s, and 12.65 w μm.

The minor side-product, retention time 26 min, isolated by glpc showed ir absorption at 5.75 μm (OAc), and its nmr spectrum (chloroform-*d*) showed two equal singlets at τ 8.59 and 8.65 (CMe_2), two three-proton singlets τ 7.88 and 7.96, and a six-proton multiplet at 5.5–6.5; no signals near 7.5 (C≡CH) or 3.3 were present.

3-*O*-Acetyl-4,5-*O*-isopropylidene-1-pentene-D-*erythro*(and D-*threo*)-3,4,5-triol (4 and 9).—The epimeric mixture of pentyne derivatives **3** and **8** (1.0 g) in ethyl acetate (50 ml) was shaken with Lindlar catalyst[8] (300 mg) and quinoline (three drops) under hydrogen at 19 psi for 0.5 hr.[20] The catalyst was filtered, the filtrate was washed twice with cold 0.1 *N* hydrochloric acid and then with water, and the dried (magnesium sulfate) organic layer was evaporated to a syrupy mixture of **4** and **9**: yield quantitative; λ_{max}^{film} 5.75 (OAc), 6.08 (C=C), 7.25, 7.30 μm (CMe_2).

Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.06. Found: C, 59.86; H, 8.07.

The product (**4** and **9**) was essentially homogeneous by glpc in the system used for separation of the acetylenic derivatives **3** and **8** and was eluted as a single peak after 30 min, under conditions wherein a standard mixture of **8** and **3** was eluted after 50 and 54 min, respectively (column temperature, 190°). The nmr spectrum of the mixture of **4** and **9** eluted from the column (Figure 3) was essentially identical with that of the product before chromatography and corresponded to that expected from the sum of the spectra of the separated epimers (see below). The spectrum provided the most reliable index of purity of the alkene mixture, by the absence of the C≡C*H* signal near τ 7.4, the presence of a four-proton, low-field multiplet (H-1,1′,2,3), and the absence of a triplet at 8.78 ($J_{1,2}$ = 7.2 Hz) for the CH_3 portion of an ethyl group, that was observed in products that had been completely reduced to the saturated hydrocarbon. The saturated derivative had a glpc retention time of 28 min.

Separation of the epimers **4** and **9** could not be achieved in the glpc system employed.

A mixture of **4** and **9** was also prepared from the aldehyde **1** by vinylation with vinylmagnesium chloride,[21] under essentially the same conditions as those used to prepare the mixture of ethynyl derivatives **2** and **7**, except that the time of reaction was increased to 1 day. The resultant mixture of 4,5-*O*-isopropylidene-1-pentene-D-*erythro*(and D-*threo*)-3,4,5-triols (**5** and **10**) was acetylated by the method used for the mixture of **2** and **7**, to give a mixture of the acetylated alkene derivatives **4** and **9**, crude yield 63%. After purification by glpc to remove a side-product, the mixture of **4** and **9** was identical by glpc

(17) This boiling point was given incorrectly in ref 2a.

(18) Analabs, Inc., Hamden, Conn.

(19) Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

(20) The length of time required for this reduction varied from one batch of catalyst to another. When the nmr spectrum of the reaction product indicated that some acetylene was still present, the reduction was continued for a longer time. Further reduction to the saturated derivative took place slowly at extended times of reaction, as revealed by nmr, but in all experiments it was possible to select a time at which reduction to the alkene was complete, but no further reduction had taken place.

(21) H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint, and R. Cserr, *J. Org. Chem.*, **22**, 1602 (1957).

retention time, nmr spectrum, and mass spectrum with the mixture of **4** and **9** produced by hemihydrogenation of the acetylenic derivatives **3** and **8**. The side-product, retention time 26 min, was identical by nmr spectroscopy with the low-boiling side-product formed in the preparation of **3** and **8**.

3-*O*-Acetyl-4,5-*O*-isopropylidene-1-pentene-D-*erythro*-3,4,5-triol (4).—To a solution of the pure acetylene derivative **3** (113 mg) in ethyl acetate (55 ml) was added freshly prepared Lindlar catalyst[8] (70 mg) and quinoline (three drops) and the mixture was shaken under hydrogen (19 psi) for 0.5 hr. The product was isolated by the procedure described for the mixture of **4** and **9**, to give **4** in a yield of 82 mg (72%); the nmr (chloroform-*d*) spectrum showed peaks at τ 3.81–4.89 (four-proton multiplet, H-1,1′,2,3), 5.64–6.28 (three-proton multiplet, H-4,5,5′), 7.93 (three-proton singlet, OAc), 8.60, 8.67 (three-proton singlets, CMe_2). The product was homogeneous by glpc.

3-*O*-Acetyl-4,5-*O*-isopropylidene-1-pentene-D-*threo*-3,4,5-triol (9).—The pure acetylene derivative **8** (100 mg) was reduced by the procedure used for its epimer, to give **9**; nmr (chloroform-*d*) peaks were at τ 4.13–4.83 (four-proton multiplet, H-1,1′,2,3), 5.71–6.33 (three-proton multiplet, H-4,5,5′), 7.90 (three-proton singlet, OAc), 8.58, 8.65 (three-proton singlets, CMe_2). The product was homogeneous by glpc.

Mass Spectrometric Studies on 3, 8, 4, and 9.—Samples were introduced[22] by a direct inlet system; temperature of the ion source was 190°; ionizing energy, 70 eV. Substance **3** gave *m/e* 183 (56) ($M^+ - Me$), 127 (115), 108 (31), 101 (100) ($CH_2OCMe_2CH{=}O^+$), 89 (90), 83 (8), 82 (8), 81 (16), 80 (13), 79 (13), 78 (13), 77 (8), 70 (18), 61 (15), 60 (13), 59 (15) (Me_2CO^+H), 58 (25) (Me_2CO^+), 57 (8), 56 (7), 55 (13), 54 (15), 53 (13), 52 (8), 51 (20), 50 (13), 44 (270) ($O{=}C{=}O^+$), 43 (205) ($MeCO^+$), 42 (43) ($CH_2{=}C{=}O^+$), 41 (30), 39 (25) ($HC{\equiv}CCH_2^+$), 29 (19), 15 (30).

Substance **8** gave *m/e* 184 (10), 183 (77) ($M^+ - Me$), 123 (9), 111 (11), 102 (7), 101 (100) ($CH_2OCMe_2CH{=}O^+$), 83 (5), 82 (4), 81 (16), 80 (4), 79 (4), 78 (4), 77 (4), 73 (11), 72 (14), 61 (14), 60 (50), 59 (18) (Me_2COH^+), 58 (24) (Me_2CO^+), 57 (4), 56 (4), 55 (8), 54 (3), 53 (10), 52 (6), 51 (7), 50 (5), 49 (3), 45 (6), 44 (145) ($O{=}C{=}O^+$), 43 (363) ($MeCO^+$), 42 (37) ($CH_2{=}C{=}O^+$), 41 (21), 39 (16) ($HC{\equiv}C{-}CH_2^+$), 29 (13), 15 (23).

A mixture of **4** and **9** gave *m/e* 185 (29) ($M^+ - Me$), 159 (38), 101 (100) ($CH_2OCMe_2CH{=}O^+$), 86 (10), 84 (14), 83 (29), 73 (12), 72 (27), 67 (10), 61 (20), 59 (34) (Me_2COH^+), 58 (44) (Me_2CO^+), 57 (18), 56 (12), 55 (18), 45 (48), 44 (221) ($O{=}C{=}O^+$), 43 (287) ($MeCO^+$), 42 (33) ($CH_2{=}C{=}O^+$), 41 (41) ($CH_2{=}CH{-}CH_2^+$), 31 (287), 30 (30), 29 (181), 15 (85).

Degradation of 3-*O*-Acetyl-4,5-*O*-isopropylidene-1-pentyne-D-*threo*-3,4,5-triol (8).—A stream of ozonized oxygen was passed through a solution of **8** (118 mg) in carbon tetrachloride (25 ml) for 7 hr at 0°. The solution was added to water (30 ml) and the mixture was evaporated to give 2-*O*-acetyl-3,4-*O*-isopropylidene-D-threonic acid as a colorless syrup. This product was heated in 1 *N* hydrochloric acid for 1 hr at 100°, and the solution was evaporated to give a light brown syrup, yield 43 mg. Thin layer chromatography of this syrup on microcrystalline cellulose,[23] with 18:3:1:4 ethyl acetate–acetic acid–formic acid–water as developer and indication with silver nitrate–sodium hydroxide,[24] revealed a major component, R_f 0.64, identical in mobility to a reference sample of D-threono-1,4-lactone[25] (**14**) and clearly differentiated from D-erythrono-1,4-lactone[23,25] (**11**, R_f 0.54). Minor, slower moving components (R_f 0.36 and 0.18) were also observed; components having similar characteristics were observed when a sample of the authentic lactone **14** was heated with acid.

Degradation of 3-*O*-Acetyl-4,5-*O*-isopropylidene-1-pentyne-D-*erythro*-3,4,5-triol (3).—A sample of **3** (100 mg) was ozonized, and the resultant 3-*O*-acetyl-3,4-*O*-isopropylidene-D-erythronic acid was hydrolyzed, by essentially the same procedure used for conversion of **8** into **14**. The product had the same chromatographic characteristics as a reference sample of D-erythronolactone[23,25] (**11**), R_f 0.54, and no component corresponding to a threonolactone was observed.

Degradation of 3-*O*-Acetyl-4,5-*O*-isopropylidene-1-pentene-D-*erythro*-3,4,5-triol (4).—Ozonized oxygen was passed for 1 hr through a solution of **4** (82 mg) in ethyl acetate (20 ml) at room temperature. The solution was diluted to 50 ml with ethyl acetate, ozone was removed by partial evaporation of the solution, a small amount of Adams' catalyst (PtO_2) was added, and the solution was shaken for 0.5 hr under 1 atm of hydrogen. The solution was filtered and evaporated to give a residue of 2-*O*-acetyl-3,4-*O*-isopropylidene-*aldehydo*-D-erythrose (**12**). To this product was added water (1 ml) and sodium borohydride (50 mg), the mixture was kept for 3.5 hr at room temperature, and then acetic acid was added to bring the pH to 5. The solution was decationized by passage through a small column of Amberlite IR-120 (H^+) ion-exchange resin and the column was washed with water and with methanol. The combined effluent was evaporated and the residue was heated in 1 *N* hydrochloric acid (25 ml) for 1 hr at 100°. The solution was then coevaporated twice with propyl alcohol and 15 times with methanol, the residue was dissolved in water (10 ml), and the solution was decolorized with activated carbon and evaporated to give a clear syrup, yield 20 mg. Tlc of this product on microcrystalline cellulose,[23] with 40:11:19 butyl alcohol–ethanol–water as developer and silver nitrate–sodium hydroxide[24] as indicator revealed a major component (R_f 0.5) chromatographically indistinguishable from erythritol, but the system did not permit clear distinction of erythritol and threitol. Paper electrophoresis of the tetritols in a pH 5 molybdate buffer[11] gave a clear separation of erythritol ($M_{glucitol}$ 1.0) and threitol ($M_{glucitol}$ 0.5), and the degradation product gave a single migrating zone, $M_{glucitol}$ 1.0, detected with silver nitrate–sodium hydroxide,[24] that was indistinguishable from that of a reference sample of erythritol; no component having the mobility of a reference sample of D-threitol was present. A minor, nonmigrating component, having the chromatographic characteristics of glycerol, was also present.

p-Nitrobenzoylation of the product in pyridine solution gave erythritol tetrakis(*p*-nitrobenzoate), mp 246–247°, undepressed on admixture with an authentic sample that had been prepared essentially by the procedure of Unrau.[26] The product gave the following X-ray powder diffraction data: 11.36 w, 8.75 w, 5.63 s (2), 4.95 m, 4.60 w, 4.17 s (1), 3.80 vw, 3.57 w, 3.48 w, 3.39 vw, 3.24 m, 3.18 w, 3.10 vw, 3.02 m.

Anal. Calcd for $C_{32}H_{22}O_{16}N_4$: C, 53.48; H, 3.09; N, 7.80. Found: C, 53.42; H, 3.23; N, 7.91.

Degradation of 3-*O*-Acetyl-4,5-*O*-isopropylidene-1-pentene-D-*threo*-3,4,5-triol (9).—The alkene **9** was degraded by ozonolysis to give 2-*O*-acetyl-3,4-*O*-isopropylidene-*aldehydo*-D-threose (**15**), with subsequent borohydride reduction and hydrolysis, by the procedure described for the 3-epimer (**4**) of **9**. The product gave a single migrating component, $M_{glucitol}$ 0.5, indistinguishable by paper electrophoresis in pH 5 molybdate buffer[11] from authentic samples of D(or L)-threitol, and contained no component having the mobility of erythritol. A nonmigrating component, having the chromatographic characteristics of glycerol, was observed as a side-product. *p*-Nitrobenzoylation of the product gave a derivative having mp 219°, undepressed on admixture with an authentic sample[26] of D-threitol tetrakis(*p*-nitrobenzoate).

4,5-*O*-Isopropylidene-1-pentyne-D-*erythro*-3,4,5-triol (2).—A solution of the 3-acetate **3** (476 mg) in absolute methanol (10 ml) was treated with a catalytic amount of sodium methoxide and the mixture was kept for 1 hr at room temperature. A small piece of Dry Ice was then added, the solvent was evaporated, and the residue was extracted with chloroform (50 ml). The extract was filtered through magnesium sulfate and evaporated to give **2** as a colorless syrup, yield 351 mg (94%): λ_{max}^{film} 2.92 (OH), 3.05 (C≡CH), 4.71 (C≡C), 7.23 μm (CMe_2); nmr (chloroform-*d*), τ 5.50–6.01 (four-proton multiplet, H-3,4,5,5′), 6.42 (one-proton singlet, disappears on deuteration, OH), 7.42 (one-proton doublet, $J_{1,3}$ = 2.0 Hz, H-1), 8.52, 8.60 (three-proton singlets, CMe_2).

4,5-*O*-Isopropylidene-1-pentyne-D-*threo*-3,4,5-triol (7).—The 3-acetate **8** (137 mg) was saponified by the procedure used for conversion of **3** into **2**, to give **7** as a colorless syrup, yield

(22) Measurements were made with an AEI-MS9 mass spectrometer by courtesy of Dr. R. Dougherty and Mr. C. R. Weisenberger of this department.

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(25) E. Hardegger, K. Kreis, and H. El Khadem, *Helv. Chim. Acta*, **34**, 2343 (1951).

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102 mg (94%): λ_{max}^{film} 2.89 (OH), 3.05 (C≡CH), 4.73 (C≡C), 7.23 μm (CMe_2); nmr (chloroform-*d*), τ 5.55–6.05 (four-proton multiplet, H-3,4,5,5′), 6.60 (broad singlet, disappears on deuteration, OH), 7.45 (one-proton doublet, $J_{1,2}$ = 1.7 Hz, H-1), 8.51, 8.60 (three-proton singlets, CMe_2).

3-*O*-(3,5-Dinitrobenzoyl)-4,5-*O*-isopropylidene-1-pentyne-D-*erythro*-3,4,5-triol (17).—To a solution of compound **2** (63 mg) in dry pyridine (3 ml) was added 3,5-dinitrobenzoyl chloride (100 mg), and the mixture was stirred for 8 hr at room temperature. Ice and water (50 ml) were then added, and after 45 min the crystalline product was filtered, washed with water, and dried, yield 78 mg (56%). The product was recrystallized twice from absolute methanol to give **17** as small white needles: mp 133–133.5°; $[\alpha]^{23}D$ +50 ± 1° (*c* 2, chloroform); λ_{max}^{KBr} 3.05 (C≡CH), 4.70 (C≡C), 5.78 (C=O), 6.12, 6.48, 6.83, 13.72 (aryl), 7.41 μm (CMe_2); nmr (chloroform-*d*), τ 1.80 (three-proton singlet, aryl protons), 4.16 (one-proton quartet, $J_{1,3}$ = 2.4 Hz, $J_{3,4}$ = 3.8 Hz, H-3), 5.4–6.1 (three-proton multiplet, H-4,5,5′), 7.29 (one-proton doublet, H-1), 8.58 (six-proton singlet, CMe_2); X-ray powder diffraction data, 11.48 m, 8.04 m, 6.71 m, 5.79 w, 5.54 w, 5.18 w, 4.93 w, 4.67 m, 4.40 m, 4.04 s (1), 3.78 w, 3.44 vw, 3.33 w, 3.01 w, 2.92 w, 2.76 w.

Anal. Calcd for $C_{15}H_{14}N_2O_8$: C, 51.43; H, 4.03; N, 8.00. Found: C, 51.52; H, 4.29; N, 8.17.

3-*O*-(3,5-Dinitrobenzoyl)-4,5-*O*-isopropylidene-1-pentyne-D-*threo*-3,4,5-triol (18).—Compound **7** (110 mg) was acylated with 3,5-dinitrobenzoyl chloride (200 mg) in pyridine (3 ml) by the procedure used for preparation of **17**. The crude product was recrystallized from methanol, yield 179 mg (75%), mp 128–129°. Further recrystallization gave **18** as long, colorless needles: mp 133.5–134.5°; $[\alpha]^{24}D$ −31.5 ± 1° (*c* 1.5, chloroform); λ_{max}^{KBr} 3.03 (C≡CH), 4.67 (C≡C), 5.71 (C=O), 6.09, 6.41, 6.83, 13.70 (aryl), 7.39 μm (CMe_2); nmr (chloroform-*d*), τ 1.7 (three-proton singlet, aryl protons), 4.16 (one-proton quartet, $J_{1,3}$ = 2.2 Hz, $J_{3,4}$ = 7.3 Hz, H-3), 5.4–6.1 (three-proton multiplet, H-4,5,5′), 7.29 (one-proton doublet, H-1), 8.58 (six-proton singlet, CMe_2); X-ray powder diffraction data, 13.00 vs (1), 8.34 m, 7.38 m, 6.81 w, 6.24 w, 5.40 s, 4.85 vs (2), 4.67 w, 4.48 w, 4.23 s, 4.00 w, 3.74 m, 3.62 w, 3.45 m, 3.28 w, 3.15 w.

Anal. Calcd for $C_{15}H_{14}N_2O_8$: C, 51.43; H, 4.03; N, 8.00. Found: C, 51.38; H, 4.09; N, 8.36.

A mixture of the epimers **17** and **18** melted over the range 93–124°.

Registry No.—**1,** 15186-48-8; **2,** 4688-33-4; **3,** 4978-99-8; **4,** 15215-76-6; **7,** 4 957-71-5; **8,** 4688-51-1; **9,** 15215-80-2; **17,** 15215-78-8; **18,** 15215-79-9; erythritol tetrakis (*p*-nitrobenzoate), 15275-61-3.

The Structure of Osotriazoles of the Sugars. Conformational and Configurational Correlations of the Polyhydroxyalkyl Chain

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The phenylosotriazoles of the five-carbon sugars having the L-*erythro* and D-*threo* configurations, the six-carbon sugars having the D-*arabino*, D-*lyxo*, and L-*xylo* configurations, and their 6-deoxy analogs having the L-*lyxo* and L-*arabino* configurations have been correlated by nmr spectroscopy in methyl sulfoxide-d_6. In each example, the methine proton at C-1 of the side chain (C-3 of the original sugar) and the hydroxyl-group proton at the same position are deshielded relative to corresponding protons on the remainder of the side chain. Differences in chemical shift and vicinal proton–proton spin couplings between members of the series studied are interpreted in terms of conformational influence on the strength of intramolecular hydrogen bonding and the favored rotamer states of the side chain. The planar, zigzag arrangement of carbon atoms appears to be the favored conformation except where such an arrangement would lead to an eclipsed, 1,3 interaction of hydroxyl groups.

The favored conformation of unsubstituted, straight-chain hydrocarbons is considered to be that in which the carbon atoms adopt a planar, zigzag arrangement, in which the largest groups along each carbon–carbon bond are antiparallel.[3] The introduction of substituents along such a chain necessitates the steric and electronic requirements of these substituents to be taken into account in predicting the favored conformation. The polyhydroxyalkyl chains of acyclic sugar derivatives provide a system in which the conformational effect of oxygen atoms at adjacent carbon atoms on a chain can be studied as configurational relationships are varied. In the crystalline state it has been shown that a conformation in which the carbon atoms are essentially in the planar, zigzag arrangement is adopted in the D-gluconate ion,[4] the D-arabinonate ion,[5] and in galactitol.[6] The conformations of acyclic sugar chains in solution have not been studied extensively by physical methods. In an earlier report from this laboratory,[7] an analysis of the nmr spectrum of 2-(D-*arabino*-tetrahydroxybutyl)quinoxaline was presented. The spin couplings of the protons of the acyclic sugar chain were shown to be consistent with a planar, zigzag arrangement of the carbon chain, corresponding to attainment of minimum nonbonded interactions between the small–medium–large sets of groups at the ends of each carbon–carbon bond, as the most highly populated rotamer state.

It is not known to what extent the conformational model that accords with results on a limited number of configurational examples may be applicable to the full range of configurational possibilities. Steric effects

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