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STERIC COURSE OF TRIAZOLE FORMATION FROM ACETYLENIC SUGARS AND PHENYL AZIDE*†

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ABSTRACT

Condensation of the acetylenic sugar 1,2-dideoxy-4,5:6,7-di-*O*-isopropylidene-D-*gluco*-hept-1-ynitol (**1**) with phenyl azide gave mainly the 1-phenyl-1,2,3-triazole derivative (**5**) having the sugar chain at C-4, together with a minor proportion of the 5-substituted analogue (**6**). The D-*manno* analogue (**2**) of **1** reacted similarly, to give the corresponding 4-substituted (**13**) and 5-substituted (**14**) 1-phenyl-1,2,3-triazoles. Structures of the products were established by degrading **5** and **13** to 1-phenyl-1,2,3-triazole-4-carboxaldehyde (**11**), and **6** and **14** to 1-phenyl-1,2,3-triazole-5-carboxaldehyde (**12**). The optical rotatory behavior of the derivatives having an unsubstituted sugar chain attached to the triazole ring is in accord with the Generalized Heterocycle Rule, but the rule does not hold for some of the derivatives having substituents on the sugar chain.

INTRODUCTION

Several papers from this laboratory have described the extension of sugar chains by ethynylation of aldehydo sugar derivatives[3,4]. The configuration at the new asymmetric center formed in the Grignard reaction was established by degradation studies, and correlated with n.m.r. spin-coupling data. It has been shown[5] that phenyl azide reacts readily with acetylenic sugar derivatives to give 4-substituted 1-phenyl-1,2,3-triazoles. Such products are of interest as a route to structures of the *C*-nucleoside type, and the reaction also provides a potential method for determining the stereochemistry at the propargylic alcohol position of the acetylenic precursor by application of the rules relating optical rotation with configuration in derivatives having a chiral center attached to an aromatic heterocycle[5].

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This paper describes examples of the cycloaddition of phenyl azide to acetylenic sugar derivatives obtained by ethynylation of 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D-arabinose. The reactions lead to the 4-substituted 1-phenyl-1,2,3-triazoles, with the concurrent formation of the corresponding 5-substituted isomers as minor side-products. Structures of the products have been firmly established by degradative methods, and the validity of the Generalized Heterocycle Rule for assigning configuration at the carbon atom attached to an aromatic heterocycle has been examined.

RESULTS AND DISCUSSION

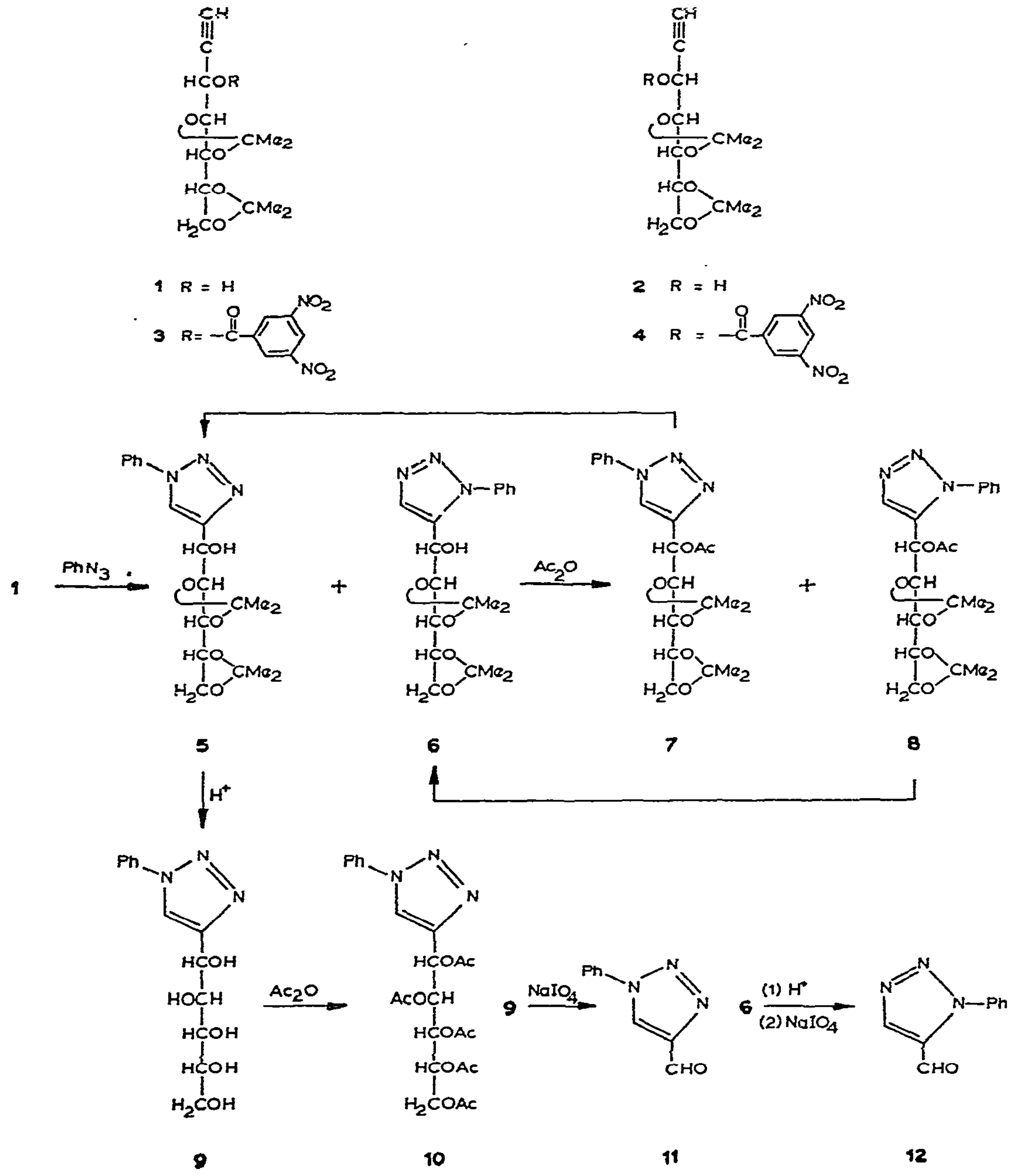
2,3:4,5-Di-*O*-isopropylidene-*aldehydo*-D-arabinose[6] was treated with ethynylmagnesium bromide according to the general procedure described[4] for the L enantiomorph. In the present work, separation of the two epimers was achieved by column chromatography, and the crystalline 1,2-dideoxy-4,5:6,7-di-*O*-isopropylidene-D-*gluco*-hept-1-ynitol (**1**) and its syrupy D-*manno* epimer (**2**) were isolated in 46 and 31% yields, respectively. The products were identical with the known[4] L enantiomorphs, except for their signs of rotation. The corresponding 3-(3,5-dinitrobenzoates) (**3** and **4**) obtained from **1** and **2** were both crystalline, and identical in all characteristics, except for sign of rotation, with the known[4] L enantiomorphs. As the structures of the enantiomorphs have been securely assigned by degradative methods[4], the structures of **1**–**4** are established conclusively.

In the 3-*O*-acyl derivatives **3** and **4**, the H-3 n.m.r. signal is exposed at low field, so that $J_{3,4}$ can be readily determined. In the D-*manno* epimer (**4**), $J_{3,4}$ is 2.5 Hz as the H-3–H-4 gauche rotamers are strongly favored; the larger $J_{3,4}$ value (4.0 Hz) for the D-*gluco* epimer **3** indicates some contribution of the H-3–H-4 antiparallel rotamer to the conformational population about C-3–C-4.

Treatment of the D-*gluco* acetylene **1** with phenyl azide according to the general procedure already described[5] gave a mixture of the 1,4- and 1,5-disubstituted 1,2,3-triazoles (**5** and **6**), which could not be resolved by fractional crystallization. However, acetylation of the product gave a mixture from which the crystalline 1,4-disubstituted isomer **7** could be isolated in 54% yield, and the syrupy 1,5-disubstituted isomer **8** was obtained in 24% yield. The acetates **7** and **8** were separately deacetylated with methanolic ammonia to give the respective alcohols **5** and **6**, each obtained crystalline.

In previous studies[5] on the condensation of acetylenic sugars with phenyl azide, only one product was isolated and identified, namely, the 4-substituted 1-phenyl-1,2,3-triazole; steric considerations predict this as the favored product, and its identity was established degradatively. Formation of two isomeric, disubstituted 1,2,3-triazoles in the reaction of glycosyl azides with phenylacetylene has been reported[7]. Steric considerations in the present instance suggest that the major product (**5**) should be the 1,4-disubstituted product, with the minor product (**6**) being the 1,5-disubstituted isomer, whose formation would encounter more steric obstruction through interaction of large groups at adjacent positions on the heterocyclic ring being generated. These assignments were unequivocally confirmed by degradation.

Deacetonation of **5** gave the crystalline pentol **9**, which was further characterized as the crystalline pentaacetate **10**. Periodate oxidation of the pentol **9** gave crystalline 1-phenyl-1,2,3-triazole-4-carboxaldehyde (**11**), m.p. 98–99°, λ_{max} 247 nm, identical



with the known compound[5,8]. The minor, isomeric triazole derivative **6** was deacetonated, and the product oxidized with periodate, to give crystalline 1-phenyl-1,2,3-triazole-5-carboxaldehyde (**12**), m.p. 77–78°, λ_{max} 223 nm. In addition to the clear differences in m.p. and in the u.v. absorption maxima displayed by the two aldehydes (**11** and **12**), they showed characteristic differences in their n.m.r. spectra; the phenyl signal for **11** was a broad multiplet, whereas that for **12** was a sharp singlet. These differences were noted by García-López *et al.*[7] for other disubstituted 1,2,3-triazoles, and were suggested by them as a means for differentiating 1,4- and 1,5-disubstitution. The aryl rings in **11** are presumably coplanar, whereas steric interactions between the phenyl group and the aldehyde group in **12** may force the phenyl group out of the plane of the triazole ring, giving rise to the observed u.v.- and n.m.r.-spectral differences.

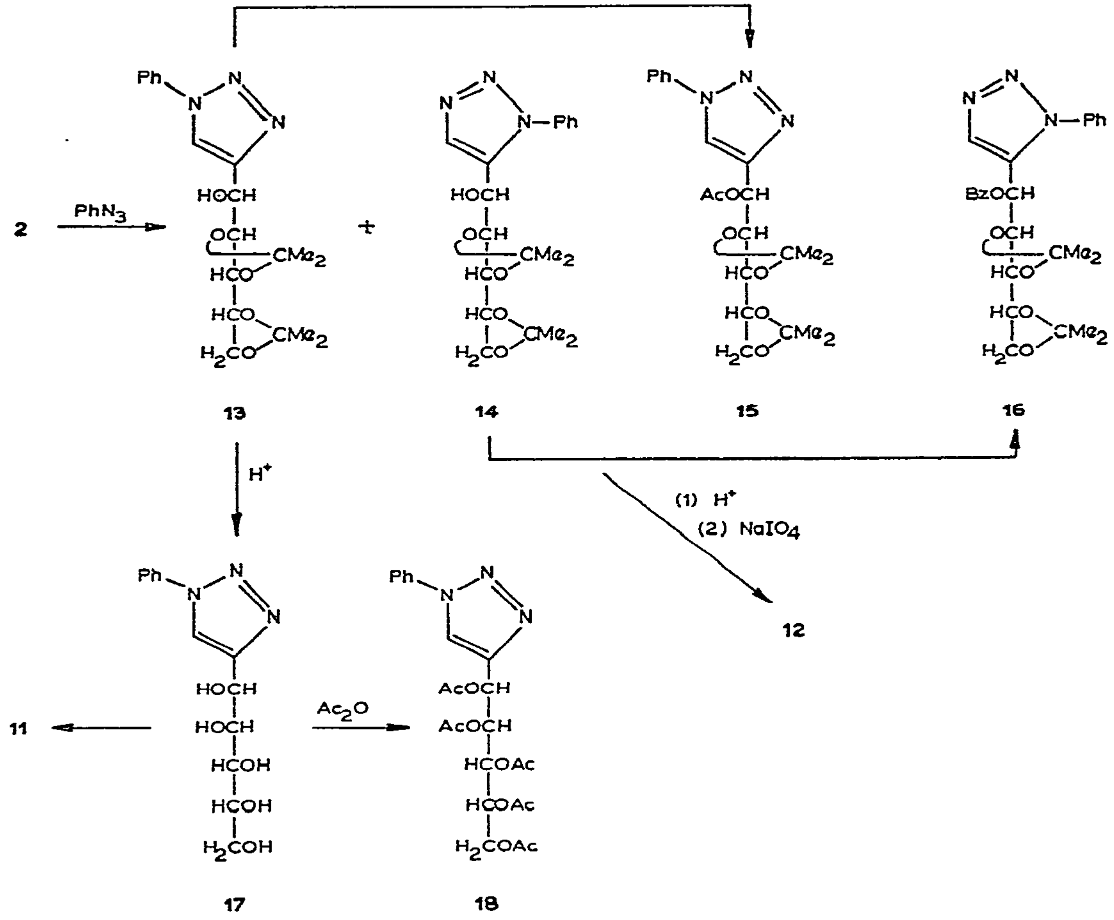
The mass spectra of **11** and **12** showed similar patterns of fragmentation, but the peak at *m/e* 103 ($\mathrm{Ph{-}\overset{+}{N}{\equiv}\dot{C}}$) is much more intense in the spectrum of **11** than in that of **12**. For the former compound (**11**), the *m/e* 103 fragment can arise from the molecular ion by a direct process, whereas the –CHO group must be split off before the $\mathrm{Ph{-}\overset{+}{N}{\equiv}\dot{C}}$ ion can be formed from **12**.

The D-*manno* acetylene **2** reacted with phenyl azide to give a mixture of triazole derivatives from which the crystalline, 1,4-disubstituted isomer **13** was isolated in 66% yield; column chromatography gave the syrupy 1,5-disubstituted isomer **14** in 6% yield. The latter was characterized as its crystalline 3-benzoate **16**; and the crystalline 3-acetate (**15**) of the major product (**13**) was also prepared.

Deacetonation of **13** afforded the crystalline pentol **17**, whose pentaacetate (**18**) was also crystalline. Periodate oxidation of the pentol **17** gave crystalline 1-phenyl-1,2,3-triazole-4-carboxaldehyde (**11**), thus confirming the assigned substitution-mode in the precursor **17** and its derivatives **13**, **15**, and **18**. Similarly, the minor, isomeric triazole (**14**) was deacetonated and the product oxidized by periodate, giving rise to 1-phenyl-1,2,3-triazole-5-carboxaldehyde (**12**), thus confirming the structure assigned to **14** (and **16**).

This synthesis of several triazole derivatives having different substituents on the side-chain attached to the heterocyclic ring permitted examination of the validity of the rule (Generalized Heterocycle Rule)[5,9–11] that relates the optical rotation of polyhydroxyalkyl derivatives of aromatic heterocycles with the stereochemistry of the CHOH group attached directly to the heterocycle. Orienting the sugar chain in the Fischer projection with the heterocycle at the top, the rules states that the compound will be dextrorotatory (at the sodium D line) when the hydroxyl group on C-1 of the side-chain is on the right, and levorotatory when this hydroxyl group is on the left; the other chiral centers give rotatory contributions of smaller magnitude, insufficient to alter the sign of the net rotation.

General application of the rule would lead to prediction of dextrorotation of all compounds derived from **1**, and levorotation of all compounds derived from **2**. This is not the case, and several exceptions are observed. Thus, in the D-*gluco* series,



compound **8** was levorotatory, and in the D-*manno* series, the diacetal **13** and the pentaacetate **18** were dextrorotatory.

The unsubstituted derivatives **9** and **17** have positive and negative rotations, respectively, in accord with the rule. This behavior supports the view of Mills[11], who has stated that the rule is applicable only with derivatives having unsubstituted polyhydroxyalkyl chains. Extension[10] of the generalization to the peracetates appears to be invalid, in view of the behavior observed here for the pentaacetate **18**.

EXPERIMENTAL

General methods. — Solutions were evaporated under diminished pressure below 50°. Melting points were determined with a Thomas–Hoover "Unimelt" apparatus and are uncorrected. N.m.r. spectra were recorded by W. N. Rond at 100 MHz with a Varian HA-100 spectrometer, with solutions in chloroform-*d* containing tetramethylsilane as the internal standard. Mass spectra were recorded by C. R. Weisenberger with an AEI MS-902 double-focusing, high-resolution spectrometer at an ionizing potential of 70 eV, an accelerating potential of 8 kV, and a source temperature of 250°. T.l.c. was performed with 250-μm layers of Silica Gel G (E. Merck) as the adsorbent and 5:1 benzene–methanol as the developer, and zones were detected by use of 10% sulfuric acid in ethanol. Column chromatography was performed on Silica Gel 7734 (E. Merck) with an adsorbent:sample ratio of 50–100:1. Microanalyses were performed by W. N. Rond.

*1,2-Dideoxy-4,5:6,7-di-*O*-isopropylidene-*D-gluco *(and* D-manno)*-hept-1-ynitol* (**1** *and* **2**). — A solution of ethylmagnesium bromide, prepared in tetrahydrofuran (30 ml) from magnesium (1.0 g) and ethyl bromide (5 ml), was added dropwise to tetrahydrofuran (100 ml) through which a stream of acetylene was passed before, during, and after the addition. To the resultant, pink solution was added a solution of 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D-arabinose[6] (4.0 g), dropwise, with stirring. The mixture was stirred for 1 h at ~25°, and then successively washed at 0° with two 30-ml portions of saturated aqueous ammonium chloride and water. The organic phase was evaporated, and the resultant syrup, dissolved in benzene, was transferred to a column of silica gel. Elution with 17:1 benzene–ether gave the D-*gluco* epimer **1**, which crystallized upon addition of petroleum ether; yield 2.04 g (46%), m.p. 68–69° (raised to 70–71° by recrystallization), $[\alpha]_D^{22}$ $-6°$ (*c* 1.1, chloroform) (lit.[4] for the L enantiomorph, m.p. 67–69°, $[\alpha]_D^{22}$ $+6°$ in chloroform); n.m.r. spectrum superposable on that of the L enantiomorph[4].

Anal. Calc. for $C_{13}H_{20}O_5$: C, 60.91; H, 7.84. Found: C, 60.70; H. 7.79.

Continued elution of the column gave the syrupy D-*manno* epimer **2**; yield 1.36 g (31%), $[\alpha]_D^{26}$ $+27°$ (*c* 1.9, chloroform) (lit.[4] for the L enantiomorph, liquid, $[\alpha]_D^{22}$ $-24°$ in chloroform); n.m.r. spectrum superposable on that of the L enantiomorph[4].

*1,2-Dideoxy-3-*O*-(3,5-dinitrobenzoyl)-4,5:6,7-di-*O*-isopropylidene-*D-gluco*-hept-1-ynitol* (**3**). — To a solution of **1** (110 mg) in pyridine (2 ml) was added 3,5-dinitrobenzoyl chloride [prepared by heating a mixture of 3,5-dinitrobenzoic acid (0.5 g) and phosphorus pentachloride (1 g)] in pyridine (2 ml), and the resultant solution was kept for 5 h at ~25°. Ether was added, and the solution was washed successively at 0° with water, M hydrochloric acid, 0.5M sodium hydroxide, and water, dried (magnesium sulfate), and evaporated, and the residue recrystallized from benzene–petroleum ether to give **3** as fine needles; yield 115 mg (60%), m.p. 135–136°, $[\alpha]_D^{22}$ $+19.7°$ (*c* 1, chloroform) (lit.[4] for the L enantiomorph, m.p. 134.5–135.5°, $[\alpha]_D$ $-19.5°$ in chloroform); n.m.r. data: δ 9.20 (5-proton, s, Ph), 5.94 (1-proton, dd, $J_{3,4}$ 4 Hz, H-3), 4.42 (1-proton, dd, $J_{4,5}$ 6 Hz, H-4), 4.30–3.95 (4-proton, m, H-5,6,7,7′), 2.71 (1-proton, d, $J_{1,3}$ 2.3 Hz, H-1), 1.58, 1.51, 1.42, and 1.38 (3-proton, s, CMe_2).

Anal. Calc. for $C_{20}H_{22}N_2O_{10}$: C, 53.35; H, 4.92; N, 6.22. Found: C, 53.45; H, 4.93; N, 6.28.

*1,2-Dideoxy-3-*O*-(3,5-dinitrobenzoyl)-4,5:6,7-di-*O*-isopropylidene-*D-manno*-hept-1-ynitol* (**4**). — The D-*manno* epimer **2** (77 mg) was treated with 3,5-dinitrobenzoyl chloride as just described for **1**. The crystalline product **4** was recrystallized from ethanol; yield 62 mg (46%), m.p. 166–167°, $[\alpha]_D^{22}$ −1.5° (*c* 1, chloroform) (lit.[4] for the L enantiomorph, m.p. 167–167.5°, $[\alpha]_D^{22}$ +2.9° in chloroform); n.m.r. data: δ 9.20 (5-proton, s, Ph), 5.99 (1-proton, t, $J_{3,4}$ 2.5 Hz, H-3), 4.40 (1-proton, dd, $J_{4,5}$ 6 Hz, H-4), 4.35–4.00 (4-proton, m, H-5,6,7,7′), 2.71 (1-proton, d, $J_{1,3}$ 2.5 Hz, H-1), 1.56, 1.52, 1.48, and 1.40 (3-proton, s, CMe_2).

Anal. Calc. for $C_{20}H_{22}N_2O_{10}$: C, 53.35; H, 4.92; N, 6.22. Found: C, 53.08; H, 5.19; N, 6.51.

*4-(1-O-Acetyl-2,3:4,5-di-O-isopropylidene-*D-gluco*-pentitol-1-yl)-1-phenyl-1,2,3-triazole* (**7**) *and 5-(1-O-acetyl-2,3:4,5-di-O-isopropylidene-*D-gluco*-pentitol-1-yl)-1-phenyl-1,2,3-triazole* (**8**). — The ethynyl derivative **1** (1.0 g) was heated with phenyl azide[12] (1 ml) for 7 h at 95–100°, and the mixture was evaporated to a crystalline residue which was recrystallized from acetone–petroleum ether; yield 1.3 g. T.l.c. showed the product to be a mixture of the two adducts **5** and **6**. Conventional acetylation with acetic anhydride–pyridine gave a crystalline residue, which was recrystallized from benzene–petroleum ether to give pure **7** as fine needles; yield 0.78 g (48%), m.p. 127–128°, $[\alpha]_D^{26}$ +65° (*c* 1, chloroform); n.m.r. data: δ 8.07 (1-proton, s, *CH* of triazole), 7.89–7.34 (5-proton, m, Ph), 6.39 (1-proton, d, $J_{1,2}$ 4 Hz, H-1 of side-chain), 4.63 (1-proton, dd, $J_{2,3}$ 6 Hz, H-3), 4.30–3.95 (4-proton, m, H-3,4,5,5′), 2.27 (3-proton, s, OAc), 1.62, 1.56, and 1.45 (3-, 3-, and 6-proton, s, CMe_2).

Anal. Calc. for $C_{21}H_{27}N_3O_6$: C, 60.42; H, 6.51; N, 10.06. Found: C, 60.40; H, 6.52; N, 9.90.

The mother liquor from the crystallization of **7** was found (t.l.c.) to consist mainly of the isomer **8**. The solution was evaporated, the residue dissolved in benzene, and the solution transferred to a column of silica gel. Elution with 6:1 benzene–ether gave an additional 0.1 g (6%) of the crystalline isomer **7**. Further elution afforded compound **8** as a chromatographically homogeneous syrup; yield 0.4 g (24%), $[\alpha]_D^{22}$ −1.5° (*c* 1.2, chloroform). This product was characterized by deacetylation to give crystalline compound **6**.

*4-(2,3:4,5-Di-O-isopropylidene-*D-gluco*-pentitol-1-yl)-1-phenyl-1,2,3-triazole* (**5**). — Compound **7** (0.25 g) was treated with 10% methanolic ammonia (10 ml) for 5 h at ~25°. Evaporation of the solution gave a crystalline residue which was recrystallized from acetone–petroleum ether; yield 0.29 g (89%), m.p. 140–141°, $[\alpha]_D^{25}$ +2.5° (*c* 0.9, chloroform).

Anal. Calc. for $C_{19}H_{25}N_3O_5$: C, 60.78; H, 6.71; N, 11.19. Found: C, 60.55; H, 6.33; N, 11.39.

*5-(2,3:4,5-Di-O-isopropylidene-*D-gluco*-pentitol-1-yl)-1-phenyl-1,2,3-triazole* (**6**). — The syrupy triazole derivative **8** was deacetylated as described for **7**. Recrystallization from benzene–petroleum ether gave pure compound **6**; yield 275 mg (78%), m.p. 161–162°, $[\alpha]_D^{22}$ +17.3° (*c* 1, chloroform); n.m.r. data: δ 7.92 (1-proton, s, H-1 of triazole), 7.80–7.30 (5-proton, m, Ph), 4.40–3.95 (6-proton, m, H-1,2,3,4,5,5′), 1.58, 1.37, and 1.35 (6-, 3-, and 3-proton, s, CMe_2).

Anal. Calc. for $C_{19}H_{25}N_3O_5$: C, 60.78; H, 6.71; N, 11.19. Found: C, 60.96; H, 6.74; N, 11.48.

*4-(*D-gluco*-Pentitol-1-yl)-1-phenyl-1,2,3-triazole* (**9**). — To a solution of compound **5** (0.62 g) in ethanol (50 ml) was added Amberlite IR-120 (H^+) resin (5 g) and the mixture was stirred for 5 h at 60–70°. The supernatant liquor was evaporated to a crystalline residue, which was recrystallized from aqueous ethanol to give pure **9**; yield 0.31 g (66%), m.p. 190–191°, $[\alpha]_D^{22}$ +2.0° (*c* 0.8, *N,N*-dimethylformamide).

Anal. Calc. for $C_{13}H_{17}N_3O_5$: C, 52.87; H, 5.80; N, 14.22. Found: C, 52.98; H, 5.59; N, 14.05.

*4-(1,2,3,4,5-Penta-O-acetyl-*D-gluco*-pentitol-1-yl)-1-phenyl-1,2,3-triazole* (**10**). — To a solution of compound **9** (110 mg) in pyridine (2 ml) was added acetic anhydride (0.5 ml), and the mixture was kept for 18 h at ~25°. Evaporation of the mixture gave a syrup that was passed through a column of silica gel. Elution with 14:1 dichloromethane–ether gave a crystalline product which was recrystallized from benzene–petroleum ether to give pure **10**; yield 140 mg (75%), m.p. 135–136°, $[\alpha]_D^{22}$ +77° (*c* 1.1, chloroform).

Anal. Calc. for $C_{23}H_{27}N_3O_{10}$: C, 54.64; H, 5.32; N, 8.31. Found: C, 54.45; H, 5.35; N, 8.29.

1-Phenyl-1,2,3-triazole-4-carboxaldehyde (**11**). — To a suspension of the triazole derivative **9** (100 mg) in water (30 ml) was added sodium metaperiodate (500 mg), and the mixture was kept for 5 h at ~25° with occasional shaking. The mixture was then extracted with chloroform, and the extract evaporated to give the crystalline aldehyde **11**. Recrystallization from benzene–petroleum ether gave the product as long needles; yield 35 mg (60%), m.p. 98–99° (lit.[5] m.p. 99–100° and[8] 98°); λ_{max}^{EtOH} 247 nm (ε 15,100); n.m.r. data: δ 10.13 (1-proton, s, CHO), 8.60 (1-proton, s, CH of triazole), 7.88–7.52 (5-proton, m, Ph); *m/e* 173 (20, $M^{+\cdot}$), 144 (52, $M^{+\cdot} - \cdot CHO$), 117 (36), 103 (34, $Ph\text{–}\overset{+}{N}\equiv\dot{C}$), 89 (12), 77 (100, Ph^+), and 51 (52).

Anal. Calc. for $C_9H_7N_3O$: C, 62.41; H, 4.07; N, 24.26. Found: C, 62.17; H, 4.06; N, 24.07.

1-Phenyl-1,2,3-triazole-5-carboxaldehyde (**12**). — To a solution of the triazole derivative **6** (0.27 g) in ethanol (60 ml) was added Amberlite IR-120 (H^+) resin (3 g), and the mixture was stirred for 4 h at 60–70°. The supernatant liquor was evaporated to a syrup, which was treated with sodium metaperiodate as already described for compound **9**. Recrystallization of the product from benzene–petroleum ether gave the pure aldehyde **12**; yield 65 mg (51%), m.p. 77–78°; λ_{max}^{EtOH} 223 nm (ε 7,900); n.m.r. data: δ 9.94 (1-proton, s, CHO), 8.34 (1-proton, s, CH of triazole), 7.56 (5-proton, s, Ph); *m/e* 173 (25, $M^{+\cdot}$), 144 (70, $M^{+\cdot} - \cdot CHO$), 117 (42), 103 (4, $Ph\text{–}\overset{+}{N}\equiv\dot{C}$), 89 (9), 77 (100, Ph^+), and 51 (60).

Anal. Calc. for $C_9H_7N_3O$: C, 62.41; H, 4.07; N, 24.26. Found: C, 62.27; H, 4.23; N, 24.55.

*4-(2,3:4,5-Di-O-isopropylidene-*D-manno*-pentitol-1-yl)-1-phenyl-1,2,3-triazole* (**13**) *and 5-(2,3:4,5-di-O-isopropylidene-*D-manno*-pentitol-1-yl)-1-phenyl-1,2,3-triazole*

(**14**). — A mixture of the ethynyl derivative **2** (0.53 g) and phenyl azide[12] (0.5 ml) was heated for 6 h at 90–95°. Upon cooling and adding benzene and petroleum ether, the crystalline triazole derivative **13** was obtained; yield 0.51 g (66%), m.p. 161–162°, $[\alpha]_D^{24}$ +24° (*c* 0.73, chloroform).

Anal. Calc. for $C_{19}H_{25}N_3O_5$: C 60.78; H, 6.71; N, 11.19. Found: C, 60.97; H, 6.80; N, 10.97.

The mother liquors from the crystallization were found to consist mainly of the second isomer, **14**. It was purified by chromatography on a column of silica gel, and isolated as a syrup; yield 45 mg (6%), $[\alpha]_D^{24}$ −13° (*c* 0.5, chloroform).

*5-(1-O-Benzoyl-2,3:4,5-di-O-isopropylidene-*D-manno*-pentitol-1-yl)-1-phenyl-1,2,3-triazole* (**16**). —Benzoyl chloride (0.2 ml) was added to a solution of the syrupy triazole derivative **14** (100 mg) in pyridine (2 ml), and the mixture was kept for 18 h at ~25°. Water (1 ml) was then added, and the mixture was extracted with ether. The extract was washed successively at 0° with water, M hydrochloric acid, 0.5M sodium hydroxide solution, and water, dried (magnesium sulfate), and evaporated to a crystalline product that was recrystallized from benzene–petroleum ether; yield 90 mg (70%). One further recrystallization from the same mixture gave an analytical sample, m.p. 164–165°, $[\alpha]_D^{24}$ +73° (*c* 0.9, chloroform).

Anal. Calc. for $C_{26}H_{29}N_3O_6$: C, 65.11; H, 6.09; N, 8.78. Found: C, 65.32; H, 6.20; N, 8.79.

*4-(1-O-Acetyl-2,3:4,5-di-O-isopropylidene-*D-manno*-pentitol-1-yl)-1-phenyl-1,2,3-triazole* (**15**). — Acetic anhydride (0.2 ml) was added to a solution of compound **13** (0.13 g) in pyridine (2 ml), and the mixture was kept for 18 h at ~25°. Evaporation of the mixture gave crystalline **15**, which was recrystallized from benzene–petroleum ether; yield 0.11 g (80%), m.p. 115–117°, $[\alpha]_D^{22}$ −15° (*c* 0.8, chloroform).

Anal. Calc. for $C_{21}H_{27}N_3O_6$: C, 60.42; H, 6.51; N, 10.06. Found: C, 60.65; H, 6.57; N, 10.29.

*4-(*D-manno*-Pentitol-1-yl)-1-phenyl-1,2,3-triazole* (**17**). — To a solution of the triazole derivative **13** (0.91 g) in ethanol (50 ml) was added Amberlite IR-120 (H^+) resin (3 ml), and the mixture was stirred for 5 h at 70–75°. *N,N*-Dimethylformamide was then added to dissolve the white precipitate, and the resin was filtered off. The product crystallized from the filtrate on cooling; yield 0.53 g (75%), m.p. 217–219°, $[\alpha]_D^{24}$ −12.7° (*c* 0.8, *N,N*-dimethylformamide).

Anal. Calc. for $C_{13}H_{17}N_3O_5$: C, 52.87; H, 5.80; N, 14.22. Found: C, 52.96; H, 5.92; N, 14.41.

*4-(1,2,3,4,5-Penta-O-acetyl-*D-manno*-pentitol-1-yl)-1-phenyl-1,2,3-triazole* (**18**). — The triazole derivative **17** (50 mg) was acetylated as for compound **9**, to give crystalline **18**; yield 76 mg (90%), m.p. 149–151°, $[\alpha]_D^{24}$ +11° (*c* 1, chloroform).

Anal. Calc. for $C_{23}H_{27}N_3O_{10}$: C, 54.64; H, 5.32; N, 8.31. Found: C, 54.92; H, 5.04; N, 8.39.

Degradation of **17** *to* **11** *and of* **14** *to* **12**. — Periodate oxidation of compound **17** (63 mg) as described for **9** gave 1-phenyl-1,2,3-triazole-4-carboxaldehyde (**11**);

yield 24 mg (60%), m.p. 98–99°. The product was indistinguishable from that already described.

Compound **14** (90 mg) was deacetonated, and the product oxidized by periodate as already described for **6**. The product (19 mg, 46%) had m.p. 76–77° and was indistinguishable from 1-phenyl-1,2,3-triazole-5-carboxaldehyde (**12**) already described.

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