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REGIOSPECIFIC SYNTHESES OF AZIDODEOXY AND DIAZIDODIDEOXY DERIVATIVES OF METHYL α-D-ARABINOFURANOSIDE*

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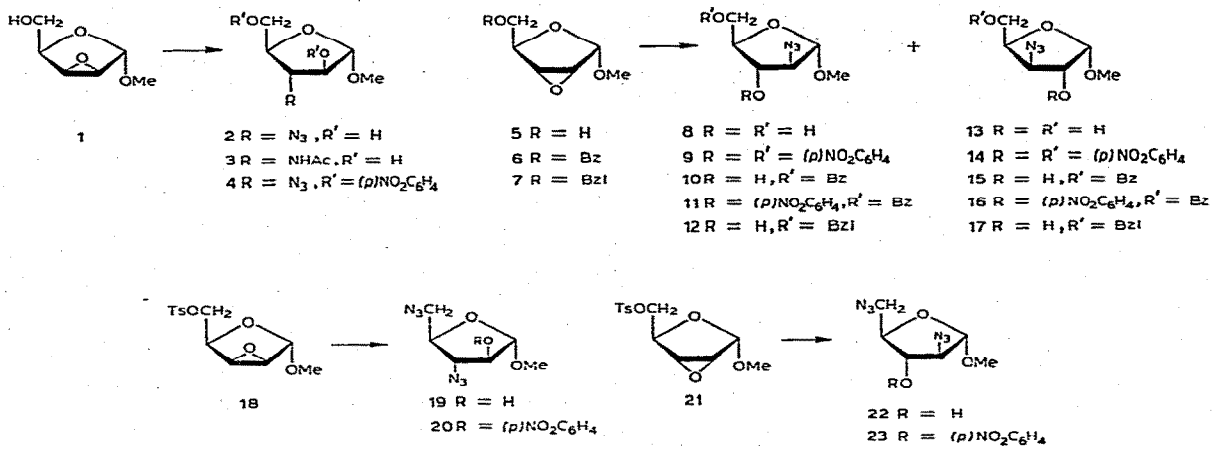
ABSTRACT

Treatment of methyl 2,3-anhydro-α-D-lyxofuranoside with ammonium azide gave only crystalline methyl 3-azido-3-deoxy-α-D-arabinofuranoside (95%). Under analogous conditions, methyl 2,3-anhydro-5-*O*-*p*-tolylsulfonyl-α-D-lyxofuranoside gave only methyl 3,5-diazido-3,5-dideoxy-α-D-arabinofuranoside (84%), isolated as its crystalline 2-*p*-nitrobenzoate; methyl 2,3-anhydro-α-D-ribofuranoside gave methyl 2-azido-2-deoxy-α-D-arabinofuranoside and methyl 3-azido-3-deoxy-α-D-xylofuranoside (3:2; 85%); methyl 2,3-anhydro-5-*O*-*p*-tolylsulfonyl-α-D-ribofuranoside gave only methyl 2,5-diazido-2,5-dideoxy-α-D-arabinofuranoside (84%), isolated as its crystalline 3-*p*-nitrobenzoate; and methyl 2,3-anhydro-5-*O*-benzoyl-α-D-ribofuranoside gave predominantly methyl 2-azido-5-*O*-benzoyl-2-deoxy-α-D-arabinofuranoside, isolated as its crystalline 3-*p*-nitrobenzoate (85%). These findings are discussed on the basis of steric and electronic effects.

INTRODUCTION

Within our search for inhibitors of Gram-negative bacterial lipopolysaccharide biosynthesis[2], we desired access to azido derivatives of D-arabinose for syntheses of azido and, eventually, amino derivatives of 3-deoxy-D-*manno*-octulosonate (KDO) *via* the Cornforth reaction[3–5]. Little has been reported[6–8] on azido derivatives of D-arabinose. A promising approach was suggested by two recent reviews[9,10] discussing, *inter alia*, epoxide cleavage of 2,3-anhydropentofuranosides by nucleophilic agents. There, it was concluded that the α-*lyxo* epoxides, without exception, yield 3-substituted *arabino* products. Moreover, it appeared that formation of 2-substituted *arabino* products is at least favored in nucleophilic epoxide cleavage of α-*ribo* epoxides[9–12]. We have, therefore, investigated the reactions of the epoxides **1** and **5**, and of their 5-substituted derivatives, **6**, **18**, and **21**, with ammonium azide.

*A preliminary account of this work has appeared[1].



DISCUSSION

Treatment of **1** with ammonium azide under the conditions given by Ali and Richardson[13] resulted in an excellent yield of the crystalline *arabino* azide **2**. Hydrogenation of **2** over palladium oxide followed by *N*-acetylation gave the known[14] acetamide **3**, the properties of which were in acceptable agreement with the reported values[14]. Considering the previous findings by other authors who had treated **1** with a variety of nucleophiles[9, 10, 12], the exclusive preference for attack at C-3 was to be expected for both steric and electronic reasons. By analogy, azide treatment of **18** gave only the *arabino* diazide **19**, isolated as its crystalline 2-*p*-nitrobenzoate **20**, in excellent yield. The *arabino* configuration of **19** was ascertained by the n.m.r. spectrum of **20** ($J_{1,2} < 1$ Hz). This spectrum is closely similar to that of **4**, the stereochemistry of which has been related to the authentic[14] *arabino* acetamide **3**.

The reaction of the *ribo* epoxide **5** with ammonium azide gave an ~3 : 2 mixture of *arabino* and *xylo* products (**8** and **13**) in 85% yield. This result agrees well with the product distribution reported by Montgomery *et al.*[11] for the reaction of **5** with ammonia. However, using ammonium azide, we do not confirm the very low yields that these authors have obtained when treating **5** with sodium azide[11]. Electronic and steric effects seem to oppose each other in the cleavage of **5** by azide ion. Whereas the electronic effect operates in favor of attack at C-3, some steric shielding of C-3 by the side chain must be considered[11,12], so that epoxide cleavage occurs mostly (and much more slowly) *via* attack at C-2. This predominance of the steric effect appears to be even more pronounced in the reaction of **21** with azide. In this case, only the *arabino* product **22** was obtained and isolated as the crystalline 3-*p*-nitrobenzoate **15** in excellent yield. The *arabino* configuration of **22** was deduced from the n.m.r. spectrum of **23** ($J_{1,2} < 1$ Hz).

As seen in the Experimental section, treatment of **5** with azide ion is not useful for a preparative access to the 2-azido derivative **8**. For this purpose, we desired a

substrate which, upon treatment with azide, would furnish the 2-azido-2-deoxy-*arabino* compound with a degree of regioselectivity similar to that obtained in the treatment of **21** with azide. To this end, we prepared the 5-*O*-benzoyl epoxide **6**, from **5**, by standard procedure in quantitative yield. Indeed, treatment of **6** with ammonium azide in dry 2-propanol resulted in a ratio of *arabino* to *xylo* products (**10** and **15**) of ~6:1, the *arabino* compound **10** being isolated as its crystalline 3-*p*-nitrobenzoate **11** in 85% yield. An analogous conversion, by use of the recently described[12] 5-*O*-benzyl epoxide **7**, gave the corresponding *arabino* and *xylo* products (**12** and **17**) in the less favorable ratio of 13:5. No crystalline products or derivatives were obtained from these reaction mixtures.

The azido derivatives **2**, **8**, **19**, and **22** of methyl α-D-arabinofuranoside are useful intermediates, leading toward biologically interesting structures. After completion of the present work we learned of the results of Buchanan and Clark[8], who obtained crystalline methyl 2-azido-2-deoxy-β-D-arabinofuranoside (the β anomer of **8**) as a by-product (2.5% yield) when treating the β anomer of **5** with ammonium azide in boiling, aqueous 2-methoxyethanol.

EXPERIMENTAL

General methods. — Melting points were determined with a Kofler hot stage and are uncorrected. Optical rotations were determined with a Perkin–Elmer 141 polarimeter. Elemental analyses were performed by Dr. J. Zak, Mikroanalytisches Laboratorium am Institut für Physikalische Chemie, Universität Wien. N.m.r. spectra were obtained with a Varian HA-100 instrument using tetramethylsilane as the internal standard; chemical shifts are reported in p.p.m. (δ) and signals are given as s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet); coupling constants are first order. Thin-layer chromatography (t.l.c.) was performed on Merck precoated plates (5 × 10 cm, layer thickness 0.25 mm, Silica gel 60 F_{254}). Spots were detected by u.v. light and by spraying with an anisaldehyde–sulfuric acid reagent[15]. Preparative t.l.c. was carried out on Merck PLC plates Silica gel 60 F_{254}, layer thickness 2 mm, 20 × 20 cm.

2,3-Anhydropentofuranosides (**1**, **5**, **18**, *and* **21**). — Compound **1** was obtained by an improved method of Baker *et al.*[14,16], **5** by a procedure recently developed in this laboratory[16], **18** by standard tosylation of **1** as described in the literature[17], and **21** by treatment of methyl 2-*O*-*p*-nitrobenzoyl-3,5-di-*O*-*p*-tolylsulfonyl-α-D-xylofuranoside with sodium methoxide in methanol[18]. The properties of **21** were in agreement with those originally reported by Goodman[19].

Methyl 3-azido-3-deoxy-α-D-arabinofuranoside (**2**). — A mixture of **1** (14.6 g), sodium azide (13 g), and ammonium chloride (12 g) was heated in a mixture of ethanol (300 ml) and water (70 ml) at gentle reflux for 72 h. The reaction was monitored by t.l.c. (2:1, v/v, benzene–ethyl acetate). When the starting material could no longer be detected, the solvent was evaporated and the semisolid residue dissolved in water (200 ml). Continuous extraction of the aqueous phase with di-

chloromethane (300 ml; 24 h) and evaporation of the organic solvent gave 18.1 g (95%) of a colorless solid, m.p. 58–61°. Crystallization from chloroform–petroleum ether gave colorless needles (14.6 g, 77%), m.p. 60–62°, $[\alpha]_D^{20}$ +156° (*c* 0.5, methanol); ν_{max}^{KBr} 2080 cm^{-1} (N_3); n.m.r. (chloroform-*d*): δ 3.36 (s, 3 H, CH_3O), 3.72 (m, 3 H, H-3, H-5,5'), 4.02 (m, 2 H, H-2, H-4), 4.62 (broad s, 1 H, OH), 4.82 (d, 1 H, $J_{1,2}$ ~2 Hz, H-1), and 5.34 (broad s, 1 H, OH).

Anal. Calc. for $C_6H_{11}N_3O_4$: C, 38.1; H, 5.8; N, 22.2. Found: C, 38.1; H, 5.8; N, 22.0.

Methyl 3-acetamido-3-deoxy-α-D-arabinofuranoside (**3**). — A solution of **2** (2.5 g) in dry ethyl acetate (50 ml) was hydrogenated over palladium oxide (25 mg) for 24 h at room temperature and atmospheric pressure. The white, gelatinous precipitate, which had formed, was dissolved by addition of ethyl acetate, the catalyst filtered off, and the solvent evaporated to leave a colorless glass still containing solvent (2.25 g, ~120%). This was dissolved in dry methanol (30 ml) and treated with acetic anhydride (2 ml) for 2 h at room temperature. Evaporation of the solvent, followed by three additions and evaporations of dry toluene gave 2.74 g (100%) of crude, solid **3**. Two recrystallizations from ethyl acetate–ethanol gave large, colorless prisms, m.p. 120–122°, $[\alpha]_D^{20}$ +131° (*c* 2, water); lit.[14] m.p. 115–116°, $[\alpha]_D^{24}$ +102° (*c* 2, water); ν_{max}^{KBr} 3355 (NH, OH), 2850 (CH_3O), 1640 (Amide I), and 1550 cm^{-1} (Amide II); n.m.r. (20 mg suspended in 500 µl of chloroform-*d*, and dimethyl sulfoxide-d_6 added dropwise until all had dissolved): δ 1.96 (s, 3 H, AcO), 3.37 (s, 3 H, CH_3O), 3.72 (d of d's, 2 H, $J_{5,OH-5}$ ~5 Hz, $J_{5,4}$ ~3.5 Hz, H-5,5'), 3.85–4.20 (m, 3 H, H-2, H-3, H-4), 4.78 (t, 1 H, temp. dep., $J_{OH-5,5'}$ ~5 Hz, OH-5), 4.84 (s, 1 H, H-1), 5.18 (d, 1 H, temp. dep., $J_{OH,2}$ ~6 Hz, OH-2), and 7.40 (broad d, $J_{NH,3}$ ~7 Hz, NH).

Anal. Calc. for $C_8H_{15}NO_5$: C, 46.8; H, 7.3; N, 6.8. Found: C, 46.7; H, 7.3; N, 6.8.

*Methyl 3-azido-3-deoxy-2,5-di-*O*-p-nitrobenzoyl-α-D-arabinofuranoside* (**4**). — This compound was prepared from **2** by standard procedure in 43% yield; m.p. 113–114° (from ethanol), $[\alpha]_D^{20}$ +3.5° (*c* 0.24, chloroform); λ_{max}^{EtOH} 257 nm (ε 31 400); n.m.r. (chloroform-*d*): δ 3.44 (s, 3 H, CH_3O), 3.97 (d of d's, 1 H, $J_{3,4}$ ~6 Hz, $J_{3,2}$ ~2 Hz, H-3), 4.31 (d of t's, 1 H, $J_{4,5,5'}$ ~4 Hz, $J_{4,3}$ ~6 Hz, H-4), 4.56 (d of d's, 1 H, $J_{5,5'}$ ~12 Hz, $J_{5,4}$ ~4 Hz, H-5), 4.72 (d of d's, 1 H, $J_{5',5}$ ~12 Hz, $J_{5',4}$ ~4 Hz, H-5'), 5.17 (s, 1 H, H-1), 5.31 (d, 1 H, $J_{2,3}$ ~2 Hz, H-2), and 8.18 (m, 8 H, nitroaromatic protons).

Anal. Calc. for $C_{20}H_{17}N_5O_{10}$: C, 49.3; H, 3.5; N, 14.4. Found: C, 49.6; H, 3.5; N, 13.7.

Methyl 2-azido-2-deoxy-α-D-arabinofuranoside (**8**) and *methyl 3-azido-3-deoxy-α-D-xylofuranoside* (**13**). — Compound[16] **5** (3.8 g) in ethanol (30 ml) was mixed with a solution of sodium azide (3.8 g) and ammonium chloride (3.2 g) in water (20 ml), and heated for 72 h at 100° (bath temperature). The solution was evaporated, the residue dissolved in water (50 ml), and continuously extracted with dichloromethane (200 ml, 24 h). Evaporation of the organic solvent, gave a colorless oil (4.19 g, 85%) which consisted of **8** (~60%) and **13** (~40%; estimated from t.l.c.

spot sizes). In t.l.c., **8** and **13** were barely separated (ethyl acetate, R_F ~0.5). Partial separation of a 500-mg sample by column chromatography (100 × 1.2 cm; Merck Silica gel 60, 230–400 mesh; 20:1 v/v chloroform–ethanol; pressure 1.5 atm) afforded 37 mg of the faster-moving component, **8** (R_F ~0.56, ethyl acetate), $[\alpha]_D^{20}$ +123° (*c* 1.4, methanol); n.m.r. (chloroform-*d*): δ 2.40–2.90 (broad s, 1 H, temp. dep., OH), 3.43 (s, 3 H, CH_3O), 3.82 (m, 2 H, H-5,5'), 3.94 (m, 1 H, H-2), 4.07 (m, 2 H, H-3, H-4), and 4.89 (d, 1 H, $J_{1,2}$ ~1 Hz, H-1).

The slower-moving component **7** (27 mg, R_F ~0.47 in ethyl acetate) showed $[\alpha]_D^{20}$ +126° (*c* 1.5 in methanol) and n.m.r. (chloroform-*d*): δ 2.13 (broad s, 1 H, OH), 2.77 (broad s, 1 H, OH), 3.44 (s, 3 H, CH_3O), 3.69 (d, 2 H, $J_{5,4}$ ~4 Hz, H-5), 3.96–4.34 (m, 3 H, H-2, H-3, H-4), and 4.88 (d, 1 H, $J_{1,2}$ ~4 Hz, H-1).

Treatment of the product mixture with *p*-nitrobenzoyl chloride in pyridine gave a mixture apparently containing two completely esterified azido sugars (probably **9** and **14**) which were inseparable by ordinary chromatographic techniques.

*Methyl 3,5-diazido-3,5-dideoxy-α-*D*-arabinofuranoside* (**19**). — To a hot, stirred solution of **18** (1 g) in ethanol (12.5 ml) was added a solution of sodium azide (895 mg) and ammonium chloride (874 mg) in water (2.3 ml). The mixture was heated under gentle reflux for 36 h, at which time **18** could no longer be detected by t.l.c. (10:1, v/v, benzene–ethyl acetate). The solution was then evaporated, the residue dissolved in chloroform, the chloroform phase washed with water, dried (magnesium sulfate), and evaporated, leaving **19** as a brownish syrup (597 mg, 84%) which was sufficiently pure for further conversions. A small portion was purified by preparative t.l.c. (10:1, v/v, benzene–ethyl acetate), $[\alpha]_D^{20}$ +188° (*c* 0.53, chloroform); $\nu_{max}^{CH_2Cl_2}$ 2090 cm^{-1} (N_3); n.m.r. (chloroform-*d*): δ 3.41 (s, 3 H, CH_3O), 3.56, 3.78, 4.14 (3 m's, total 6 H, including H-5, H-5', H-3, H-4, OH, and H-2), and 4.90 (d, 1 H, $J_{1,2}$ ~3 Hz, H-1).

*Methyl 3,5-diazido-3,5-dideoxy-2-*O*-p-nitrobenzoyl-α-*D*-arabinofuranoside* (**20**). — Compound **19** (597 mg) was treated with *p*-nitrobenzoyl chloride in pyridine to give **20** (850 mg, 84%), m.p. 70–75° (from ethyl acetate–pentane), $[\alpha]_D^{20}$ +134° (*c* 0.43, chloroform); ν_{max}^{KBr} 2090 (N_3), 1722 (C=O ester), 1521 (NO_2), 1342 (NO_2), and 1260 cm^{-1} (C–O ester); λ_{max}^{MeOH} 258 nm, ε 14 200; n.m.r. (chloroform-*d*): δ 3.40 (d of d's, 1 H, $J_{5,5'}$ ~14 Hz, $J_{5,4}$ ~4 Hz, H-5), 3.49 (s, 3 H, CH_3O), 3.79 (d of d's, 1 H, $J_{5',5}$ ~14 Hz, $J_{5',4}$ ~4 Hz, H-5'), 4.01 (d of d's, 1 H, $J_{3,4}$ ~6 Hz, $J_{3,2}$ ~2 Hz, H-3), 4.20 (d of t's, 1 H, $\delta_{4,3}$ ~6 Hz, $\delta_{4,5,5'}$ ~4 Hz, H-4), 5.21 (s, 1 H, H-1), 5.35 (d, 1 H, $J_{2,3}$ ~2 Hz, H-2), and 8.31 (m, 4 H, nitroaromatic protons).

Anal. Calc. for $C_{13}H_{13}N_7O_6$: C, 43.0; H, 3.6; N, 27.0. Found: C, 43.1; H, 3.6; N, 25.6.

*Methyl 2,5-diazido-2,5-dideoxy-α-*D*-arabinofuranoside* (**22**). — Compound **21** (1 g) was subjected to treatment with ammonium azide in the manner described for **18** to give **12** (600 mg, 84%) as a light-tan syrup which was sufficiently pure for further conversions. A sample was purified by preparative t.l.c. as described for **19**, $[\alpha]_D^{20}$ +141° (*c* 0.66, chloroform); $\nu_{max}^{CH_2Cl_2}$ 2070 cm^{-1} (N_3); n.m.r. (chloroform-*d*)

showed three ill-resolved multiplets in the range δ 3.20–5.00, among which could be discerned δ 3.43 (s, 3 H, CH_3O) and 4.93 (s, 1 H, H-1).

*Methyl 2,5-diazido-2,5-dideoxy-3-*O*-*p*-nitrobenzoyl-α-*D*-arabinofuranoside* (**23**). — Compound **22** (0.6 g) was treated with *p*-nitrobenzoyl chloride in pyridine to give **23** (0.7 g, 70%), m.p. 86–88° (from ethyl acetate–pentane), $[\alpha]_D^{20}$ +93.3° (*c* 0.92, chloroform); λ_{max}^{MeOH} 258 nm, ε 13 300; ν_{max}^{KBr} 2095 (N_3) 1716 (C=O ester), 1519 (NO_2), 1347 (NO_2), and 1280 cm^{-1} (C-O ester); n.m.r. (chloroform-*d*): δ 3.48 (s, 3 H, CH_3O), 3.58 (d of d's, 1 H, $J_{5,5'}$ ~14 Hz, $J_{5,4}$ ~4 Hz, H-5), 3.76 (d of d's, 1 H, $J_{5',5}$ ~14 Hz, $J_{5',4}$ ~4 Hz, H-5'), 4.18 (d, 1 H, $J_{2,3}$ ~2 Hz, H-2), 4.42 (d of t's, 1 H, $J_{4,5,5'}$ ~4 Hz, $J_{4,3}$ ~5 Hz, H-4), 5.22 (d of d's, $J_{3,2}$ ~2 Hz, $J_{3,4}$ ~5 Hz, H-3), and 8.29 (m, 4 H, nitroaromatic protons).

Anal. Calc. for $C_{13}H_{13}N_7O_6$: C, 43.0; H, 3.6; N, 27.0. Found: C, 43.1; H, 3.7; N, 26.0.

*Methyl 2-azido-5-*O*-benzoyl-2-deoxy-3-*O*-*p*-nitrobenzoyl-α-*D*-arabinofuranoside* (**11**). — Compound **6** (4.41 g), ammonium chloride (2.3 g), and sodium azide (3.5 g) were heated to reflux in dry 2-propanol for 7 days with exclusion of moisture. The solvent was then evaporated, and the residue dissolved in chloroform (200 ml), washed with water (2 × 200 ml), dried (magnesium sulfate), filtered, and evaporated again to leave 5.15 g (100%) of a slightly yellow syrup. This was directly *p*-nitrobenzoylated by standard procedure to give 7.80 g (100%) of a yellow syrup consisting of **11** and **16** in an estimated (t.l.c.) ratio of 6 : 1. Crystallization from ethanol afforded **11** (total yield, 6.64 g, 85%), m.p. 96–98° (from ethanol), $[\alpha]_D^{20}$ +86.4° (*c* 0.28, chloroform); λ_{max}^{MeOH} 257 (ε 16 500) and 230 nm (ε 20 000); ν_{max}^{KBr} 2100 (N_3), 1722, 1714 (C=O esters), 1522 (NO_2), 1345 (NO_2), and 1265 cm^{-1} (C-O esters); n.m.r. (chloroform-*d*): δ 3.46 (s, 3 H, CH_3O), 4.20 (d of d's, 1 H, $J_{2,1}$ ~1 Hz, $J_{2,3}$ ~2 Hz, H-2), 4.51–4.87 (m, 3 H, H-4, H-5,5'), 5.04 (d, 1 H, $J_{1,2}$ ~1 Hz, H-1), 5.38 (d of d's, 1 H, $J_{3,2}$ ~2 Hz, $J_{3,4}$ ~4.5 Hz, H-3), 7.25–7.65 and 8.00–8.40 (2 m's, 9 H, arom. protons of benzoyl and *p*-nitrobenzoyl groups).

Anal. Calc. for $C_{20}H_{18}N_4O_8$: C, 54.3; H, 4.1; N, 12.7. Found: C, 54.1; H, 4.0; N, 12.4.

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