Epoxide ring opening of methyl 2,3-anhydro-4-azido-4-deoxy-pentopyranosides

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Epoxide ring opening reactions of methyl 2,3-anhydro-4-azido-4-deoxy-pentopyranosides with hydroxide ion and methoxide ion are described. The products obtained by reactions of the epoxides with hydroxide ion are related, by preparation of their 2,3-di-*O*-methanesulfonyl derivatives, to known compounds or their enantiomers. Opening of the α-D(and L)-*ribo* epoxides with methoxide ion gave monomethylated products which were characterized by nuclear magnetic resonance analysis of their acetates. The relative yields of the two major products obtained in each case are not accounted for, in some cases, by consideration of only steric and inductive effects.

L'auteur décrit les réactions de rupture du noyau cyclique d'époxyde des méthyl 2,3-anhydro-4-azido-4-deoxy-pentopyranosides par l'ion hydroxyde et l'ion méthoxyde. Les produits obtenus par réaction des époxydes avec l'ion hydroxyde se rattachent à des produits connus ou à leurs antipodes optiques par la voie de leurs dérivés 2,3-di-*O*-méthanesulfonylés. La rupture du noyau cyclique de l'α-D(et L)-*ribo* époxyde avec l'ion méthoxyde donne des produits monométhylatés qui ont été déterminés grâce à l'analyse par résonance magnétique nucléaire de leurs acétates. L'abondance relative des deux principaux produits obtenus dans chaque cas suggère que d'autres facteurs que ceux de simple probabilité et d'induction, influençant la direction de rupture du noyau cyclique, devraient être pris en considération pour l'étude des sucres d'époxydes.

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The stereochemistry of ring-opening reactions of sugar epoxides is well established (1). For epoxides attached to pyranose rings, *trans*-diaxial opening by nucleophilic reagents is a general rule, with few exceptions, because of the geometric requirements of the transition state for the S_N2 reaction (2–5). Thus, opening of epoxides attached to pyranose rings whose conformations are stabilized, e.g. by acetal formation, gives mainly one product (1). However, the direction of ring opening of epoxides of monocyclic pyranoses, where it is possible for the reaction to occur in either half-chair conformation of the six-membered ring, is not easily rationalized, since it is dependent upon the steric effects (4, 6),[2] the electronic effects of neighboring substituents (5, 6),[2] and perhaps also an effect exerted by the oxygen in the ring (4).

In a continuation of an investigation of the synthesis of 4-acetamido-4-deoxy-pentoses (7), methyl 2,3-anhydro-4-azido-4-deoxy-pentopyranosides (8) were caused to react with aqueous potassium hydroxide. It was noted that the reaction of methyl 2,3-anhydro-4-azido-4-deoxy-β-L-ribopyranoside with hydroxide ion (7) and methoxide ion (8) gave derivatives of L-xylose as the predominant product, in agreement with the persistent formation of xylose derivatives from methyl 2,3-anhydro-β-D(and L)-ribopyranosides by reaction with a variety of nucleophiles (1). However, predominant opening at C-3 of carbohydrate 2,3-epoxides is not always observed (9, 10), which must indicate that there are directive influences other than simple steric and polar inductive effects.

The enantiomeric (L and D) methyl 2,3-anhydro-4-azido-4-deoxy-α-lyxopyranosides (I and III), upon reaction with aqueous potassium hydroxide, gave the corresponding (L and D) methyl 4-azido-4-deoxy-α-xylopyranosides (VII and IX) and methyl 4-azido-4-deoxy-α-arabinopyranosides (VIII and X) in an approximate yield ratio of 1:4. Nucleophilic attack has occurred predominantly at C-3. However,

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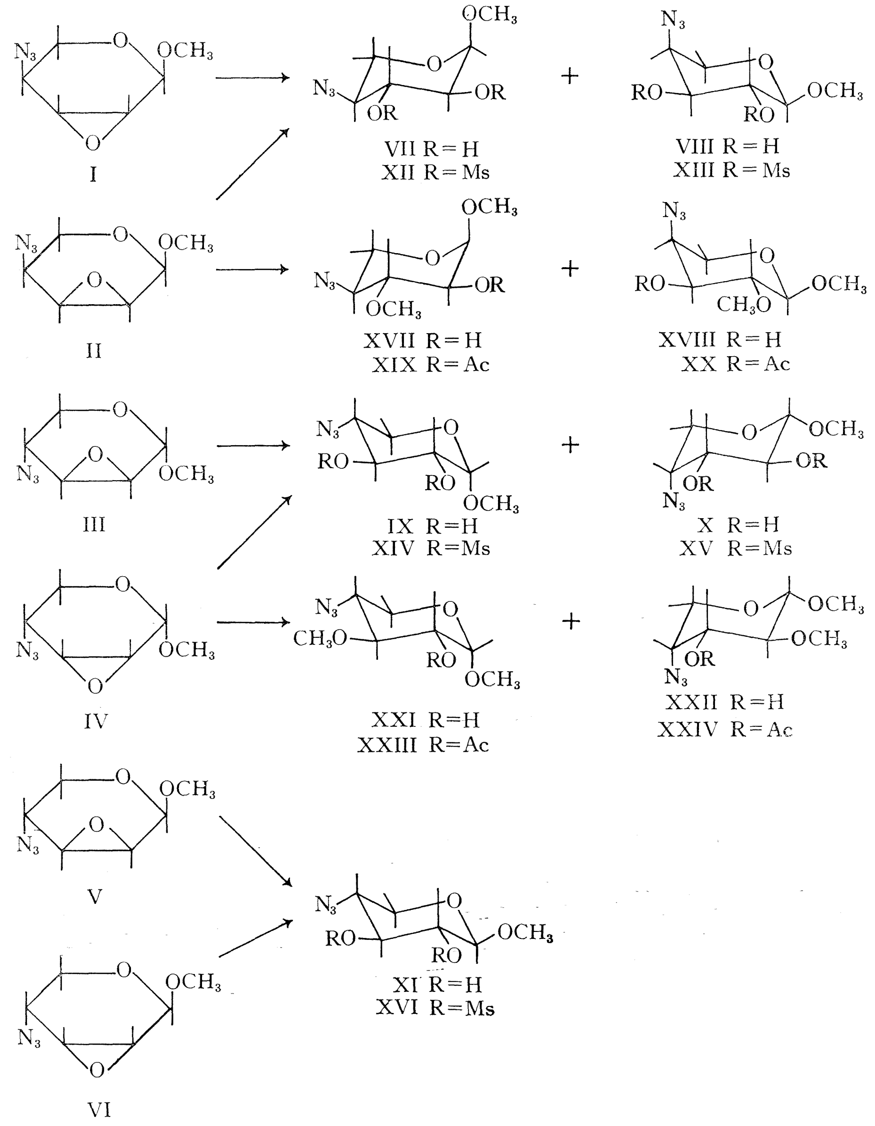


the isomeric 2,3-anhydro-α-ribopyranosides (II and IV) gave the same two products as the corresponding lyxopyranosides (i.e. L or D), but in a yield ratio of very nearly 1:1. The extent of opening at C-2 for the *α-ribo* epoxides is unexpected because of the electron-withdrawing effect of the acetal function at C-1, which would favor epoxide ring opening at C-3 (3, 5, 6).[2] Steric effects would appear to be of little importance for the 2,3-anhydro-α-ribopyranosides, since there is one quasi-axial and one quasi-equatorial substituent in either half-chair conformation of the six-membered ring. Also, the results from the α-lyxosides would preclude an unusually strong polar inductive effect of the azido group (11).

The production of the same two products from the opening of the isomeric *ribo* and *lyxo* epoxides leaves no doubt that *trans* opening of the epoxide ring has occurred. The major products from the epoxide opening of the α-glycosides were isolated by resolution of the reaction product mixture by silica gel column chromatography. A number of minor products were sometimes observed upon examination of the reaction mixtures by thin-layer chromatography (t.l.c.), but were not characterized. Clearly, the nature of the major products formed from the epoxide opening reaction in the *lyxo* series under the conditions employed rules out a significant contribution from a mechanism involving neighboring-group participation by the azido group (12, 13).

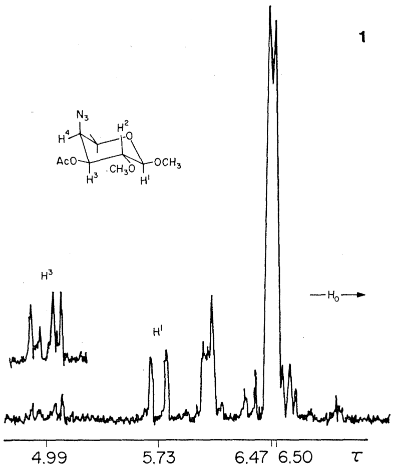
Proof of structure of the methyl 4-azido-4-deoxy-α-pentopyranosides was provided by the preparation of their 2,3-di-*O*-methanesulfonyl derivatives. The dimesylates (XIII and XIV) of methyl 4-azido-4-deoxy-α-L-arabinopyranoside (VIII) and of methyl 4-azido-4-deoxy-α-D-xylopyranoside (IX) were identical with the previously prepared compounds (8). The dimesylates (XII and XV) of methyl 4-azido-4-deoxy-α-L-xylopyranoside (VII) and of methyl 4-azido-4-deoxy-α-D-arabinopyranoside (X) had the same melting points as, and specific rotations of opposite sign to, their D and L enantiomers (XIV and XIII, respectively).

The reaction of methyl 2,3-anhydro-4-azido-4-deoxy-β-D-lyxo(and -ribo)pyranosides (V and VI) with aqueous potassium hydroxide gave the same major product, methyl 4-azido-4-deoxy-β-D-xylopyranoside (XI). The dimesylate (XVI) of XI has been prepared previously (8). It may be noted that there is predominant opening at C-2 of the β-D-*lyxo* epoxide (V), in contrast to the α anomer (III), which gave epoxide ring opening mainly at C-3. Changing the anomeric configuration in the *ribo* series (IV and VI) has a less profound effect on the proportion of products, opening occurring predominantly at C-3 for the β anomer but at C-2 and C-3 in nearly equal proportions for the α anomer.

The products of the opening of the epoxide ring of methyl 2,3-anhydro-4-azido-4-deoxy-α-L (and D)-ribopyranosides (II and IV) with methoxide ion were also investigated. These monomethylated derivatives were isolated from the reaction of methyl 4-azido-4-deoxy-2,3-di-*O*-methanesulfonyl-α-L-arabinopyranoside (XIII) and methyl 4-azido-4-deoxy-2,3-di-*O*-methanesulfonyl-α-D-xylopyranoside (XIV) with sodium methoxide in methanol (8). Monitoring of the reactions by t.l.c. clearly showed that the methylated products were derived from the *ribo* epoxides. Methyl 4-azido-4-deoxy-3-*O*-methyl-α-L-xylopyranoside (XVII, crystalline) and methyl 4-azido-4-deoxy-2-*O*-methyl-α-L-arabinopyranoside (XVIII, an oil) were obtained from XIII by chromatography of the crude product mixture on a silica gel column. Significantly, the relative yield of XVII and XVIII was similar to that of VII and VIII obtained by reaction of methyl 2,3-anhydro-4-azido-4-deoxy-α-L-ribopyranoside (II) with aqueous potassium hydroxide. Proof of structure of XVII and XVIII was provided by nuclear magnetic resonance (n.m.r.) analysis of their monoacetates (XIX and XX, respectively), which were both obtained as oils.

The n.m.r. spectrum of XX (Fig. 1) showed a doublet at τ 5.73 ($J_{1,2}$ 6.5 c.p.s.) which was assigned to H-1. A one-proton quartet at τ 4.99 ($J_{2,3}$ 8.5 c.p.s., $J_{3,4}$ 3.5 c.p.s.) was assigned to H-3. Since the resonance of this proton is downfield, the acetoxy group is at C-3. The relatively large couplings between H-1 and H-2 and between H-2 and H-3 indicate that these pairs of hydrogens are disposed *trans* diaxially. The small coupling between H-3 and H-4 indicates that H-4 is equatorial. Since the configuration of the methoxyl group is known, it follows that XX is methyl 3-*O*-acetyl-4-azido-4-deoxy-2-*O*-methyl-α-L-arabinopyranoside.

The structure of the other methylated product may be assigned as methyl 4-azido-4-deoxy-3-*O*-methyl-α-L-xylopyranoside (XVII) if normal *trans* opening of the epoxide ring is assumed. The n.m.r. spectrum of XVII (Fig. 2) showed a doublet at τ 5.22 ($J_{1,2}$ 3 c.p.s.) which was assigned to H-1. The relatively small coupling between H-1 and H-2 is consistent with H-1 being equatorial and H-2 axial in an α-L-*xylo* configuration in the 1C comformation. In the n.m.r. spectrum of the acetate (XIX, Fig. 2) H-2 has moved downfield, so that H-1 and H-2 now have



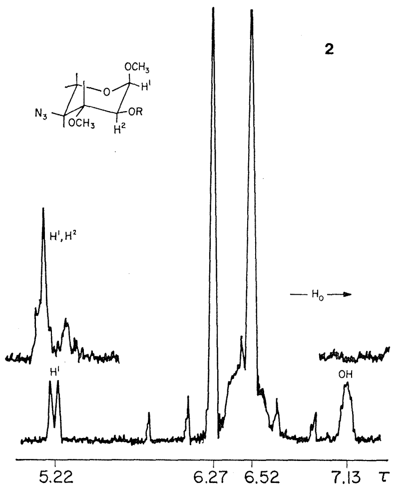


FIG. 1. Partial n.m.r. spectrum of methyl 3-*O*-acetyl-4-azido-4-deoxy-2-*O*-methyl-α-L-arabinopyranoside (XX). The insert shows the signal for H-3 at higher gain.

FIG. 2. Partial n.m.r. spectrum of methyl 4-azido-4-deoxy-3-*O*-methyl-α-L-xylopyranoside (XVII). The insert shows the complex signal for H-1 and H-2 of methyl 2-*O*-acetyl-4-azido-4-deoxy-3-*O*-methyl-α-L-xylopyranoside (XIX).

very similar chemical shifts, causing a complex two-proton signal at τ 5.25. Since the resonance of H-2 in XIX is shifted downfield from its position in XVII, the acetoxy group is at C-2. XIX is therefore methyl 2-*O*-acetyl-4-azido-4-deoxy-3-*O*-methyl-α-L-xylopyranoside. Analogous results were obtained for the reaction of the D-ribose derivative IV with sodium methoxide.

EXPERIMENTAL

Solutions were concentrated under reduced pressure below 50° with a rotating evaporator. Melting points were determined on a Fisher–Johns apparatus and are uncorrected. Optical rotations were measured in chloroform solution at 23 ± 3° with a Hilger standard polarimeter. The infrared spectra obtained for the compounds described were consistent with the assigned structures. Nuclear magnetic resonance spectra were measured in $CDCl_3$ solution with a Varian A-60 spectrometer; chemical shifts were measured with 6% tetramethylsilane in chloroform as an external standard. Thin-layer chromatography was carried out on silica gel; after irrigation, the plates were air dried and the spots located by spraying the chromatograms with a 5% solution of sulfuric acid in ethanol and heating the plates at 120°.

Column chromatography was carried out with Davison silica gel (grade 950, 60–200 mesh). A glass column was packed with dry silica gel. The substance to be fractionated was dissolved in acetone, and sufficient dry silica gel was added to the solution so that a free-flowing powder was obtained upon evaporation of the solvent. This dry powder was introduced onto the top of the silica gel column and gently packed. The irrigant was then introduced and a head of not more than 1 cm maintained until the irrigant emerged from the botton of the column. Fractions (5–10 ml) of the eluate were collected, and carbohydrate material was detected by testing samples from the fractions by t.l.c.

Reaction of Methyl 2,3-Anhydro-4-azido-4-deoxy-pentopyranosides with Aqueous Potassium Hydroxide

A mixture of the epoxide and an aqueous solution of potassium hydroxide (5%) was boiled under reflux. The reaction was monitored by t.l.c. (irrigant: ethyl acetate – light petrol (1:3 v/v)). When all of the starting material had been consumed, the solution was cooled, neutralized (H_2SO_4), and continuously extracted with chloroform for 36 h. The chloroform extract was dried ($MgSO_4$) and concentrated to a brown crystalline mass. This mixture was then subjected to silica gel column chromatography (irrigant: ethyl acetate–light petrol (1:1 v/v)). The appropriate effluent fractions were pooled and concentrated, and the crystalline residue was recrystallized from ethyl acetate – light petrol or chlrorform – light petrol. The epoxides which underwent this reaction were the methyl 2,3-anhydro-4-azido-4-deoxy-pentopyranosides having the α-L, α-D, and β-D *lyxo* and *ribo* configurations. The two major products in each case had the *xylo* and *arabino* configurations. A typical experiment is as follows. Methyl 2,3-anhydro-4-azido-4-deoxy-α-L-ribopyranoside (II, 5.1 g) and aqueous potassium hydroxide (5%, 60 ml) were boiled under reflux for 3 h. Chromatography of the mixture of

TABLE I

Methyl 4-azido-4-deoxy-pyranoside	Melting point	$[\alpha]_D$	% yield from methyl 2,3-anhydro-4-azido-4-deoxy-pyranoside		Found (%)*		
			ribo	*lyxo*	C	H	N
α-L-*xylo* (VII)	80–81.5°	−218° (*c*, 1.45)	41	10	38.1	5.7	22.3
α-L-*arabino* (VIII)	96–96.5°	−23° (*c*, 1.08)	33	40	38.0	5.6	22.1
α-D-*xylo* (IX)	79–80.5°	+210° (*c*, 1.58)	38	14	38.2	6.1	22.1
α-D-*arabino* (X)	95.5–96.5°	+22° (*c*, 2.50)	35	75	38.2	6.0	22.4
β-D-*xylo* (XI)	87–88.5°	−30° (*c*, 1.00)	40		38.3	5.9	22.4

*Anal. Calcd. for $C_6H_{11}N_3O_4$: C, 38.1; H, 5.8; N, 22.2

products gave three main fractions (in order of elution): (*a*) a mixture (0.35 g) of at least five substances (t.l.c. evidence) which showed strong absorption for hydroxyl and azido functions in the infrared spectrum, but was not investigated further; (*b*) methyl 4-azido-4-deoxy-α-L-xylopyranoside (VII, 2.3 g); and (*c*) methyl 4-azido-4-deoxy-α-L-arabinopyranoside (VIII, 1.85 g).

The percentage yields and physical constants of the products are shown in Table I.

The reaction mixtures of the β-D-*ribo* and β-D-*lyxo* epoxides were examined by t.l.c., and both showed one major product and a trace of a second. The reaction mixtures were thus combined for work-up (chloroform extraction, concentration, and fractional recrystallization). A specimen of the component present in trace amounts was obtained in less than a 4% yield. It melted at 108–109° and was probably methyl 4-azido-4-deoxy-β-D-arabinopyranoside (cf. the L enantiomer (7)), but was not investigated further.

Reaction of the Methyl 4-Azido-4-deoxy-pentopyranosides with Methanesulfonyl Chloride

To a solution of the azido derivative in pyridine, cooled in an ice bath, was added dropwise 2 moles of methanesulfonyl chloride. The solution was left at room temperature for several hours and was then poured into 5 volumes of ice water. The crystalline precipitate was collected and recrystallized from ethanol.

The methyl 4-azido-4-deoxy-2,3-di-*O*-methanesulfonyl-pyranosides having the α-L-*arabino* (XIII), α-D-*xylo* (XIV), and β-D-*xylo* (XVI) configurations were identical in all respects with the previously prepared compounds (8).

Methyl 4-azido-4-deoxy-2,3-di-O-methanesulfonyl-α-L-xylopyranoside (XI) melted at 117.5–118.5° and had $[\alpha]_D$ −118° (*c*, 1.95).

Anal. Calcd. for $C_8H_{15}N_3O_8S_2$: C, 27.8; H, 4.4; N, 12.2; S, 18.6. Found: C, 27.9; H, 4.4; N, 12.2; S, 18.7.

Methyl 4-azido-4-deoxy-2,3-di-O-methanesulfonyl-α-D-arabinopyranoside (XV) melted at 124.5–125.5° and had $[\alpha]_D$ −3.2° (*c*, 1.85).

Anal. Calcd. for $C_8H_{15}N_3O_8S_2$: C, 27.8; H, 4.4; N, 12.2; S, 18.5. Found: C, 27.6; H, 4.7; N, 11.8; S, 18.5.

Preparation of Methyl 4-Azido-4-deoxy-3-O-methyl-α-L-xylopyranoside and Methyl 4-Azido-4-deoxy-2-O-methyl-α-L-arabinopyranoside from Methyl 4-Azido-4-deoxy-2,3-di-O-methanesulfonyl-α-L-arabinopyranoside

Methyl 4-azido-4-deoxy-2,3-di-*O*-methanesulfonyl-α-L-arabinopyranoside (8) (39.5 g) was dissolved in hot methanol (400 ml) containing sodium methoxide (7.5 g of sodium metal). The solution was boiled under reflux for 45 min. The reaction mixture was cooled, neutralized (CO_2), diluted with 1 volume of water, and concentrated to remove most of the methanol. The aqueous residue was extracted with chloroform, the extract was dried ($MgSO_4$) and filtered, and the filtrate was concentrated to a light-brown oil. Treatment of the oil with ethanol caused the crystallization of starting material (8.3 g), which was collected by filtration. The filtrate was concentrated to a brown oil (12 g). Examination of the oil by t.l.c. revealed four components, the two faster moving of which were epoxides. It was established in preliminary monitoring experiments by t.l.c. that the two slower moving products were derived from the predominant epoxide, namely, methyl 2,3-anhydro-4-azido-4-deoxy-α-L-ribopyranoside (II).

The mixture was resolved by silica gel column chromatography. Irrigation with light petrol – ethyl acetate (4:1 v/v) gave the epoxides in a total yield of 8 g (these have been described (8)). Continued irrigation with light petrol – ethyl acetate (1:1 v/v) gave (in order of elution) XVII and XVIII.

Methyl 4-Azido-4-deoxy-3-O-methyl-α-L-xylopyranoside (XVII)

XVII was obtained as a crytalline solid (1.6 g) which, after recrystallization from chloroform–heptane, melted at 85–86° and had $[\alpha]_D$ −249° (*c*, 2.125); n.m.r.: τ 5.22 (one-proton doublet, $J_{1,2}$ 3 c.p.s., H-1), 6.27 and 6.52 (three-proton singlets, methoxyls), and 7.13 (one-proton singlet, disappears on deuteration, OH).

Anal. Calcd. for $C_7H_{13}N_3O_4$: C, 41.4; H, 6.4; N, 20.7. Found: C, 41.3; H, 6.1; N, 20.5.

Methyl 4-Azido-4-deoxy-2-O-methyl-α-L-arabinopyranoside (XVIII)

XVIII was obtained as an oil (0.9 g). An analytical sample was provided by vacuum distillation, and the distillate had $[\alpha]_D$ $-68°$ (c, 1.63); n.m.r.: τ 5.59 (one-proton doublet, $J_{1,2}$ 5.5 c.p.s., H-1) and 6.48 and 6.52 (three-proton singlets, methoxyls).

Anal. Calcd. for $C_7H_{13}N_3O_4$: C, 41.4; H, 6.4; N, 20.7. Found: C, 41.3; H, 6.4; N, 20.6.

XVIII was contaminated in the latter stages of the fractionation with starting material, which was freed of XVIII by crystallization from ethanol, 1.0 g of starting material being collected.

Methyl 2-O-Acetyl-4-azido-4-deoxy-3-O-methyl-α-L-xylopyranoside (XIX)

XVII was acetylated in pyridine solution with acetic anhydride in the ususal manner. The acetate XIX was obtained as an oil and was purified by vacuum distillation. It had $[\alpha]_D$ $-204°$ (c, 2.83); n.m.r.: τ 5.25 (two-proton multiplet, H-1 and H-2), 6.41 and 6.62 (three-proton singlets, methoxyls), and 7.85 (three-proton singlet, acetyl protons); n.m.r. (benzene): τ 5.68 (two-proton multiplet, H-1 and H-2), 7.12 and 7.49 (three-proton singlets, methoxyls), and 8.76 (three-proton singlet, acetyl protons).

Anal. Calcd. for $C_9H_{15}N_3O_5$: C, 44.1; H, 6.1; N, 17.1. Found: C, 43.9; H, 5.9; N, 17.1.

Methyl 3-O-Acetyl-4-azido-4-deoxy-2-O-methyl-α-L-arabinopyranoside (XX)

XVIII was acetylated in pyridine solution with acetic anhydride in the usual manner. The acetate XX was obtained as an oil and was purified by vacuum distillation. It had $[\alpha]_D$ $-3.5°$ (c, 1.45); n.m.r.: τ 4.99 (one-proton quartet, $J_{2,3}$ 8.5 c.p.s., $J_{3,4}$ 3.5 c.p.s., H-3), 5.73 (one-proton doublet, $J_{1,2}$ 6.5 c.p.s., H-1), 6.47 and 6.50 (three-proton singlets, methoxyls), and 7.83 (three-proton singlet, acetyl protons).

Anal. Calcd. for $C_9H_{15}N_3O_5$: C, 44.1; H, 6.1; N, 17.1. Found: C, 44.1; H, 5.8; N, 17.1.

Preparation of Methyl 4-Azido-4-deoxy-3-O-methyl-α-D-xylopyranoside and Methyl 4-Azido-4-deoxy-2-O-methyl-α-D-arabinopyranoside from Methyl 4-Azido-4-deoxy-2,3-di-O-methanesulfonyl-α-D-xylopyranoside

Methyl 4-azido-4-deoxy-2,3-di-*O*-methanesulfonyl-α-D-xylopyranoside (8) (XIV, 47.1 g) was dissolved in hot methanol (400 ml) containing sodium methoxide (7.2 g of sodium metal). The solution was boiled under reflux for 20 min. The reaction was worked up as for the reaction of XIII, 23.2 g of starting material being recovered. The reaction was repeated with XIV (23.2 g), methanol (200 ml), and sodium (3.5 g), and the solution was boiled under reflux for 1 h. After work-up, 5.5 g of starting material was recovered. The two syrupy residues were combined (20.5 g). Examination of this syrup revealed five components, one of which was the starting material. Again, preliminary monitoring experiments by t.l.c. showed that the two faster moving components were epoxides and the two slower moving products were derived from the predominant *ribo* epoxide.

Fractionation of the product mixture by silica gel column chromatography (irrigant: light petrol – ethyl acetate (4:1 v/v)) gave the pure epoxides III and IV in a total yield of 15.4 g (these have previously been described (8)). Continued irrigation with light petrol – ethyl acetate (1:1 v/v) gave a mixture of the two remaining products and starting material. Most of the starting material (XIV, 1.0 g) was removed by crystallization from ethanol. The mother liquors were concentrated to a syrup (3.1 g) and refractionated on a silica gel column (irrigant: light petrol – ethyl acetate (1:1 v/v)). Fractions *a*, *b*, and *c*, were collected.

(a) Methyl 4-Azido-4-deoxy-3-O-methyl-α-D-xylopyranoside (XXI)

XXI was obtained as a crystalline solid (1.3 g) and was shown to be homogeneous by t.l.c. It was recrystallized from chloroform – light petrol, melted at 85.5–86°, and had $[\alpha]_D$ $+244°$ (c, 1.43); n.m.r.: τ 5.20 (one-proton doublet, $J_{1,2}$ 3.5 c.p.s., H-1) and 6.24 and 6.49 (three-proton singlets, methoxyls).

Anal. Calcd. for $C_7H_{13}N_3O_4$: C, 41.4; H, 6.4; N, 20.7. Found: C, 41.5; H, 6.4; N, 20.6.

(b) A mixture of XXI and XXII (0.6 g).

(c) Methyl 4-Azido-4-deoxy-2-O-methyl-α-D-arabinopyranoside (XXII)

XXII was obtained as a colorless oil (1.0 g). An analytical sample was provided by vacuum distillation. It had $[\alpha]_D$ $+73°$ (c, 1.70); n.m.r.: τ 5.61 (one-proton doublet, $J_{1,2}$ 5.5 c.p.s., H-1) and 6.40 and 6.45 (three-proton singlets, methoxyls).

Anal. Calcd. for $C_9H_{13}N_3O_4$: C, 41.4; H, 6.4; N, 20.7. Found: C, 41.2; H, 6.3; N, 20.6.

Methyl 2-O-Acetyl-4-azido-4-decxy-3-O-methyl-α-D-xylopyranoside (XXIII)

XXI was acetylated in pyridine solution with acetic anhydride in the usual manner. The 2-acetate XXIII was obtained as a colorless oil and was purified by vacuum distillation. It had $[\alpha]_D$ $+206°$ (c, 1.50); n.m.r.: τ 5.22 (two-proton multiplet, H-1 and H-2), 6.42 and 6.63 (three-proton singlets, methoxyls), and 7.86 (three-proton singlet, acetyl protons).

Anal. Calcd. for $C_9H_{15}N_3O_5$: C, 44.1; H, 6.1; N, 17.1. Found: C, 44.3; H, 6.2; N, 17.9.

Methyl 3-O-Acetyl-4-azido-4-deoxy-2-O-methyl-α-D-arabinopyranoside (XXIV)

XXII was acetylated as usual and gave the 3-acetate XXIV as an oil which, after vacuum distillation, had $[\alpha]_D$ $+3°$ (c, 1.5); n.m.r.: τ 4.99 (one-proton quartet, $J_{2,3}$ 8.5 c.p.s., $J_{3,4}$ 3.0 c.p.s., H-3), 5.71 (one-proton doublet, $J_{1,2}$ 6.5 c.p.s., H-1), 4.48 and 5.0 (three-proton singlets, methoxyls), and 7.86 (three-proton singlet, acetyl protons).

Anal. Calcd. for $C_9H_{15}N_3O_5$: C, 44.1; H, 6.1; N, 17.1. Found: C, 43.9; H, 6.1; N, 16.9.

REFERENCES

1. F. H. Newth. Quart. Rev. London, **13**, 30 (1959).
2. S. Peat. Advan. Carbohydrate Chem. **2**, 37 (1946).

3. R. C. Cookson. Chem. Ind. London, 223 (1954); 1512 (1954).
4. S. J. Angyal. Chem. Ind. London, 1230 (1954).
5. R. E. Parker and N. S. Isaacs. Chem. Rev. **59**, 737 (1959).
6. J. Langstaff. M.Sc. Thesis, Queen's University, Kingston, Ontario. 1964.
7. A. J. Dick and J. K. N. Jones. Can. J. Chem. **43**, 977 (1965).
8. A. J. Dick and J. K. N. Jones. Can. J. Chem. **44**, 79 (1966).
9. G. Charalambous and E. Percival. J. Chem. Soc. 2443 (1954).
10. G. Casini and L. Goodman. J. Am. Chem. Soc. **85**, 235 (1963).
11. J. H. Boyer and F. C. Canter. Chem. Rev. **54**, 1 (1954).
12. A. Streitwieser, Jr. and S. Pulver. J. Am. Chem. Soc. **86**, 1587 (1964).
13. S. Hanessian. Carbohydrate Res. **1**, 178 (1965).