Preparation and Reaction of Partially Benzylated 2-Azido-2-deoxy-L-xylopyranose†

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2-Azido-3,4-di-O-benzyl-2-deoxy-L-xylopyranose (XV) was prepared. Oxidation of XV with methyl sulfoxide and acetic anhydride was examined.

It was described in the previous paper of this series¹⁾ that 2-azido-3,4,6-tri-O-benzyl-2-deoxy-D-altropyranose had been prepared and oxidized with methyl sulfoxide and acetic anhydride to afford 2-azido-3,4,6-tri-O-benzyl-2-deoxy-D-allono-1,5-lactone with a concomitant inversion of the azido group at C-2. It should be reasonable to assume that the azido group inverted from axial to equatorial attachment in Cl(D) conformation of the hexopyranose although the unequivocal conformational analysis could not be achieved.

Pentopyranose derivatives generally are in more flexible conformation than hexopyranose derivatives are, because pentopyranoses lack the hydroxymethyl group at C-5*. Therefore, it is interesting to know what products partially benzylated 2-azido-2-deoxy-pentopyranose gives on oxidation with dimethyl sulfoxide and acetic anhydride. It is especially meaningful to choose partially benzylated 2-azido-2-deoxy-L-xylopyranose as a pentopyranose derivative in connection with our present project directed towards the synthesis of polyoxins, a novel group of antibiotics, since polyoxins contain 2-amino-2-deoxy-L-xylonic acid (polyoxamic acid) as a constituent structure.⁴⁾

This paper deals with the preparation of 2-azido-3, 4-di-O-benzyl-2-deoxy-L-xylopyranose (XV) and its oxidation with methyl sulfoxide and acetic anhydride. In a prelimi-

nary experiment, it was unsuccessful to prepare 2-azido-2-deoxy-L-xylofuranose derivative from 2-O-methanesulfonyl derivative of methyl 3-O-benzyl-5-O-methoxycarbonyl-L-lyxofuranoside⁵⁾ by substitution of the sulfonate with azido ion.**

Difficulty of the introduction of an azido group to C-2 of the aldopentose derivative prompted us to employ 3-azido-3-deoxy-hexose derivative as a starting material and to cleave it between C-1 and C-2 to 2-azido-2-deoxypentose derivative. The employed material, 3-azido-3-deoxy-1,2: 5,6-di-O-isopropylidene- β -L-idofuranose (V), had been synthesized in syrupy state by Brimacombe *et al.*⁷⁾ via several reaction-intermediates including 1,2: 5,6-di-O-isopropylidene- β -L-talofuranose (III) and its 3-O-tosylate (IV). As the reaction scheme taken by Brimacombe *et al.* did not seem to secure the supply of a large quantity of III, we developed a new pathway to III. 3-O-Benzyl-1,2-O-isopropylidene- β -L-talofuranose (I)⁸⁾ was treated with dry acetone and anhydrous cupric sulphate to afford 3-O-benzyl-1,2: 5,6-di-O-isopropylidene- β -L-talofuranose (II) in good yield. Removal of benzyl group of II by hydrogenolysis with palladium on carbon (10%) as catalyst resulted in the concomitant loss of isopropylidene group. A trace of acid contained in the catalyst might cause the migration of 1,2-O-isopropylidene group to 2, 3 position and the following hydrolysis of

† Syntheses with Azido Sugars. Part VI. Part V see reference 1).

* The hydroxymethyl group at C-5 in a hexopyranose greatly contributes to its favored conformation.^{2,3)}

** It is well known with aldopyranose derivatives that polar effect of two oxygen atoms at C-1 interferes the substitution on C-2 with a charged nucleophile.⁶⁾ This will be the case in this furanose derivative.

FIG. 1.

the group during or after the migration.* In order to prevent the migration, the hydrogenolysis was attempted in the presence of a base. The hydrogenolysis with palladium on carbon, however, did not proceed at all in the presence of sodium acetate.

Successful hydrogenolysis of II was achieved in liquid ammonia with sodium metal to give III in good yield. After III had been tosylated according to Brimacombe *et al.*,⁷⁾ the resulting 3-O-tosylate (IV) was treated with sodium azide in an improved way to afford V in crystalline state. NMR spectrum of V did not reveal a well-resolved pattern for the first order analysis but addition of tris(dipivalomethanato) europium made it possible to assign whole protons. (Fig. 2)

* A similar acid-lability of 1,2-O-isopropylidene group having *cis* hydroxyl group on the contiguous carbon has been encountered in the other cases.^{5,9)}

5,6-O-Isopropylidene group of V was selectively hydrolyzed with aqueous acetic acid in two ways. The resulting 3-azido-3-deoxy-1,2-O-isopropylidene-L-idofuranose (VI) was tritylated in an usual way to afford 6-O-trityl derivative (VII). The hydroxyl group at C-5 of VII was then benzylated with benzyl chloride and potassium hydroxide to give crystalline 3-azido-5-O-benzyl-3-deoxy-1,2-O-isopropylidene-6-O-trityl-β-L-idofuranose (VIII). Simultaneous removal of the isopropylidene and trityl groups from VIII was attempted in aqueous isopropanol with sulfuric acid but it was unsuccessful because of the low solubility of VIII in such aqueous media. Therefore, two steps of reactions consisting of methanolysis and hydrolysis of the resulting methyl glycoside were carried out. Thus, VIII was treated with methanolic hydrogen chloride at room temperature to afford an

FIG. 2. NMR Spectra (100 MHz) of 3-Azido-3-deoxy-1,2:5,6-di-O-isopropylidene- β -L-idofuranose (V) in Carbon Tetrachloride Solution (48 mg in 0.7 ml).

Lower spectrum, the normal spectrum: Upper spectrum, the spectrum after addition of tris (dipivalomethanato) europium (11.25 mg). The signals attributable to methyl protons of isopropylidene groups at 8~9 are reduced on 1/2 scale.

anomeric mixture of methyl 3-azido-5-O-benzyl-3-deoxy-L-idofuranoside (IXa and IXb). Both anomers were isolated by column chromatography and identified on the bases of their NMR spectra and optical rotations. An anomeric mixture of IX was then heated in aqueous methanol with hydrochloric acid for hydrolysis of the glycosidic bond. Unexpectedly, the reaction did not proceed to completion and IX (especially α -anomer) was detected in the reaction mixture even after 20 hr. However, IX was almost completely hydrolyzed with the same acid when the solvent was changed with aqueous isopropanol. The resulting 3-azido-5-O-benzyl-3-deoxy-L-idofuranose (X) was an unstable compound in basic (even in neutral) condition and could not be isolated because of its decomposition during neutralization with base. The fact described above prompted us to oxidize X with sodium periodate soon after acidic hydro-

lysis of IX. The oxidative cleavage of X gave two products which moved differently on thin layer chromatography. They were tentatively assigned as 2-azido-4-O-benzyl-2-deoxy-3-O-formyl-L-xylopyranose (XI) and 2-azido-4-O-benzyl-2-deoxy-L-xylopyranose (XII) produced from XI by hydrolysis of its formyl group with acid in the solvent. Those assignments were supported by the fact that the mixture of XI and XII gave only one product identified with methyl 2-azido-4-O-benzyl-2-deoxy-L-xylopyranoside (XIII) on the bases of its elemental analysis and spectral data when the mixture was treated with methanol containing dry hydrogen chloride. The hydroxyl group at C-3 of XIII was benzylated as described for the preparation of VIII to afford methyl 2-azido-3,4-di-O-benzyl-2-deoxy-L-xylopyranoside (XIV). The glycosidic linkage of XIV was hydrolyzed in acetic acid with aqueous sulfuric acid to give XV as analytically pure

syrup. For its structural confirmation, XV was catalytically reduced in the presence of hydrochloric acid to give 2-amino-2-deoxy- α -L-xylose hydrochloride (XVI), of which physical properties except the optical rotation agreed with those of the known D-enantiomer.^{10, 11)} The optical rotation of XVI has a reverse sign to that of D-enantiomer but reveals a similar mutarotation.

Oxidation of XV with methyl sulfoxide-acetic anhydride was carried out as reported previously with partially benzylated 2-azido-2-deoxy-D-altropyranose.¹⁾ Result, however, was quite different from the previous case. At least three spots overlapping each other were detected on thin-layer chromatogram of the oxidation mixture. All attempts to separate each products failed. The mixture, therefore, was roughly divided into two fractions by column chromatography in such a way as the compound corresponding to the middle spot on thin-layer chromatogram was divided into these two fractions. Both fractions had IR absorptions at 1730~1740 and 2100 cm^{-1} attributable to lactone and azido group respectively. The fastly moving fraction (major fraction) had an IR absorption at 1635 cm^{-1} but the slowly moving fraction (minor fraction) had no absorption in this area. Besides, the major fraction was positive to permanganate test for double bond. On the bases of these results, the existence of an unsaturated lactone was supposed in the major fraction. Catalytic reduction of the major fraction with palladium on carbon gave several ninhydrin-positive products.* Among those products, 2-amino-2,3-dideoxy-L-threopentonic acid (deoxy polyoxamic acid) was detected on thin-layer chromatogram in comparison with an authentic sample isolated from Polyoxin E or G.⁴⁾ From this finding, the unsaturated lactone produced by oxidation of XV was elucidated to be 2-azido-4-O-benzyl-2,3-dideoxy-L-glycero-pent-2-enono-1,5-lactone (XVII). Reduction of the minor fraction also gave several products. The *R_f*

value of one of the products on thin-layer chromatogram was identical with that of authentic polyoxamic acid isolated from polyoxins A~L (except E and G).⁴⁾ Therefore, the minor fraction was confirmed to contain 2-azido-3,4-di-O-benzyl-2-deoxy-L-xylo-1,5-lactone (XVIII).

In conclusion, oxidation of XV with methyl sulfoxide-acetic anhydride gave an unsaturated lactone XVII as major product and XVIII as minor product. One more compound was formed besides these two products. On the bases of the result reported in the previous paper,¹⁾ the third product may be an epimer of XVIII.

EXPERIMENTAL

All melting points are uncorrected. Specific rotations were measured with Perkin-Elmer 141 Polarimeter in a 1 dm tube. IR spectra were recorded with Shimadzu IRS-27 spectrometer. NMR spectra were recorded at 60 MHz with Japan Electron Optics C-60 spectrometer and at 100 MHz with Varian HA 100-D spectrometer. Column chromatography was performed with silica gel (0.05~0.20 mm; E. Merck) and the solvent systems specified.

3-O-Benzyl-1,2:5,6-di-O-isopropylidene- β -L-talofuranose (II). Anhydrous cupric sulfate (19 g) was added to a solution of I (6.5 g) in anhydrous acetone which was freshly distilled from potassium permanganate and then from Drierite (Hammond Co.). The mixture was stirred under reflux over night. After filtration, the filtrate was concentrated *in vacuo* to afford a brown syrup (7.6 g) which crystallized on standing in a refrigerator. Recrystallized twice from *n*-hexane; Yield 5.2 g (71%); mp 71~73°C, $[\alpha]_D^{19} +88.3^\circ$ ($c=1.01$, chloroform). *Anal.* Found: C, 65.31; H, 7.25. *Calcd.* for $\text{C}_{19}\text{H}_{26}\text{O}_6$: C, 65.13; H, 7.48%.

1,2:5,6-Di-O-isopropylidene- β -L-talofuranose (III). To a suspension of II (49 g) in liquid NH_3 (1.5 liter) was added sodium metal (10 g) in portions under stirring at -50° . Three hours later, ammonium chloride (20 g) was added to the mixture. After the liquid ammonia was evaporated at room temperature, the resulting residue was suspended in water (1 liter) and extracted with chloroform (1 liter). The extract was washed with water, dried over sodium sulfate and evaporated *in vacuo* to afford a pale brown syrup (III) which crystallized with agitation in a small amount of cyclohexane. Recrystallized from cyclohexane; Yield 31 g (85%); mp 79~80°C, $[\alpha]_D^{24}$

* Probably partially debenzylated compounds would be in the mixture.

+27.6° ($c=0.93$, chloroform). [literature⁷¹ mp 85°C, $[\alpha]_D +31.3^\circ$ (chloroform)]

1, 2: 5, 6-Di-*O*-isopropylidene-3-*O*-*p*-toluenesulfonyl- β -L-talofuranose (IV). This compound was prepared according to the literature.⁷¹

3-Azido-3-deoxy-1, 2: 5, 6-di-*O*-isopropylidene- β -L-idofuranose (V). To a solution of 3-tosylate (IV, 108 g) in HMPA (3 liters) was added sodium azide (262 g). The mixture was heated at 110°C for 10 hr and diluted with water (5 liters). After saturation with sodium chloride, the mixture was extracted with ether (7 liters) and the extract was dried over Na₂SO₄ and evaporated *in vacuo* to give the syrupy V (81 g) which later crystallized. Recrystallized from *n*-hexane; mp 69~71°C, $[\alpha]_D^{23} -73.9^\circ$ ($c=1.21$, chloroform); [literature⁷¹ bp 135~145°C (bath)/0.5 mmHg, $[\alpha]_D -80.4^\circ$ ($c=0.51$, chloroform)], $\nu_{\max}^{11\text{m}} \text{ cm}^{-1}$: 2100 (N₃), NMR (at 100 MHz, CCl₄ solution) τ : 6.50~5.60 (5 protons, multiplet, H-3, H-4, H-5, H-6, H-6'), 5.40 (1 proton, doublet, $J_{1,2}=4$ Hz, H-2), 4.12 (1 proton, doublet, $J_{1,2}=4$ Hz, H-1).

3-Azido-3-deoxy-1, 2-*O*-isopropylidene- β -L-idofuranose (IV).

Method A. Water (2 ml) was added dropwise to a solution of V (600 mg) in acetic acid (6 ml). The mixture was kept at 40°C for 4 hr and poured into water (30 ml).

After neutralization with excess of sodium carbonate, the mixture was evaporated *in vacuo* to dryness. After the residue was extracted with chloroform (*ca.* 100 ml), the extract was washed with a little water (*ca.* 20 ml), dried over sodium sulfate and evaporated *in vacuo* to afford the syrupy VI (400 mg, 76%), which later crystallized. Recrystallized from isopropyl ether; mp 91~4°C, $[\alpha]_D^{22} -63.1^\circ$ ($c=0.789$, chloroform). $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 3400 (OH), 2100 (N₃). *Anal.* Found: C, 44.18; H, 6.24; N, 15.98. Calcd. for C₉H₁₅O₅N₃: C, 44.08; H, 6.17; N, 17.13%.

Method B. To a solution of V (7 g) in *p*-dioxane (80 ml) was added aqueous acetic acid (50% v/v, 80 ml). The mixture was kept at 60°C for 3 days, diluted with water (200 ml) and neutralized with excess of sodium carbonate. After evaporation, the resulting residue was extracted with acetone (250 ml). The extract was evaporated *in vacuo* to give a yellow syrup which crystallized on seeding. Yield 3.8 g (63%). Recrystallized from isopropyl ether; mp 91~94°C.

3-Azido-3-deoxy-1, 2-*O*-isopropylidene-6-*O*-trityl- β -L-idofuranose (VII). Trityl chloride (1.9 g, 6.8 mmole) was added to a solution of VI (1.3 g, 5.3 mmole) in dry pyridine (10 ml) and the mixture was kept at room temperature for 4 days. After complete destruction of excess

of trityl chloride by addition of a little water, the mixture was poured into ice-water (*ca.* 250 ml) and stirred until a separated syrup solidified. The precipitate (VII) was filtered, washed with isopropyl ether and dried. Yield 2.5 g (97%). This might be used for the next benzylation without further purification. A part of the crude VII was recrystallized from isopropyl ether. mp 147~150°C; $[\alpha]_D^{21} -55.9^\circ$ ($c=1.30$, chloroform). $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 3550 (OH), 2100 (N₃), 1500 (benzene ring). *Anal.* Found: C, 69.02; H, 5.99; N, 8.82. Calcd. for C₂₈H₂₉O₅N₃: C, 68.98; H, 6.00; N, 8.62%.

3-Azido-5-*O*-benzyl-3-deoxy-1, 2-*O*-isopropylidene-6-*O*-trityl- β -L-idofuranose (VIII). A mixture of VII (950 mg), powdered potassium hydroxide (*ca.* 2 g) and benzyl chloride (5 g) was heated at 90~100°C for 2.5 hr under stirring. After the mixture was cooled, it was diluted with water (50 ml) and extracted with ether (100 ml). The extract was washed with water, dried over sodium sulfate and evaporated *in vacuo* (finally below 1 mmHg) to afford syrupy VIII, which crystallized by agitation in a little methanol. Recrystallized from methanol. Yield 1 g (89%); 105~6°C, $[\alpha]_D^{23} -67.8^\circ$ ($c=0.972$, chloroform). $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 2100 (N₃), 1500 (benzene ring). *Anal.* Found: C, 72.81; H, 6.13; N, 7.55. Calcd. for C₃₅H₃₅O₅N₃: C, 72.77; H, 6.11; N, 7.27%.

Methyl 3-azido-5-*O*-benzyl-3-deoxy- α (and β)-L-idofuranoside (IXa and IXb). Methanolic hydrogen chloride (4.5% w/v, 600 ml) was added to a suspension of VIII (31 g) in methanol (1 liter). The mixture was stirred at room temperature over night protecting from moisture, neutralized with excess of solid sodium bicarbonate and filtered. The filtrate was evaporated *in vacuo* and the resulting residue was extracted with acetone (*ca.* 700 ml). The extract was evaporated *in vacuo* to afford a brown syrup (32 g) which solidified. Methanol (*ca.* 200 ml) was added to the residue and agitated. The crystals (triphenyl carbinol or its methyl ester) were filtered off and washed with a small amount of methanol (50 ml). Combined filtrate and washings were evaporated *in vacuo* to afford a brown syrup (IXa and IXb, 20 g) which could be used for the next step (hydrolysis of the glycoside) without further purification.

A part of this syrup (700 mg) was chromatographed on silica gel (70 g) with chloroform-methanol (96:4 v/v) as eluent. Compound IXb (β -anomer) was eluted faster than IXa (α -anomer). For IXb (syrup): yield 284 mg, $[\alpha]_D^{23} +114.3^\circ$ ($c=0.867$, chloroform), $\nu_{\max}^{11\text{m}} \text{ cm}^{-1}$: 3350~3300 (OH), 2100 (N₃), 1500 (benzene ring). NMR (at 60 MHz, CDCl₃ solution) τ 5.05 (1 proton, doublet, $J_{1,2}=4.5$ Hz, H-1). *Anal.* Found: C, 54.33; H, 6.21; N, 13.09. Calcd. for C₁₄H₁₉O₅N₃: C, 54.36; H, 6.19; N, 13.58%. For IXa: yield 174 mg. Recrystallized from ethyl acetate-*n*-hexane, mp 103~

105°C, $[\alpha]_D^{21} -99.0^\circ$ ($c=0.823$, chloroform), $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3370, 3300 (OH), 2100 (N_3), 1500 (benzen ring). NMR (at 60 MHz, CDCl_3 solution) τ 5.16 (1 proton, singlet, H-1). *Anal.* Found: C, 54.19; H, 6.14; N, 13.40. Calcd. for $\text{C}_{14}\text{H}_{19}\text{O}_5\text{N}_3$: C, 54.36; H, 6.19; N, 13.58%.

Methyl 2-azido-4-O-benzyl-2-deoxy-L-xylopyranoside (XIII) via X and XI, XII. A mixture of IXa and IXb (19 g) was dissolved in isopropanol (500 ml). To the solution was added aqueous hydrochloric acid (2 N, 500 ml) and the mixture was heated under reflux for 1.5 hr with stirring. The mixture was diluted with additional hydrochloric acid (2 N, 200 ml) and heated for further 2.5 hr. After the mixture was cooled in an ice-bath, a solution of sodium periodate (12 g) in water (200 ml) was added. The mixture was stirred at 0°C for 1 hr, neutralized with sodium hydrogen carbonate to pH 5~6, filtered and washed with isopropanol. The combined filtrate and washings were concentrated *in vacuo* to the volume of several hundred ml and extracted with ethyl acetate (1.3 liter). The extract was washed with water, dried over sodium sulfate and evaporated *in vacuo* to afford a brown syrup (18.6 g) which revealed two spots on t.l.c. using chloroform-methanol (94:6 v/v). The syrup (XI and XII, 18 g) was dissolved in methanol (800 ml) containing dry hydrogen chloride (28 g). The mixture was heated under reflux for 4.5 hr, neutralized with excess of sodium hydrogen carbonate and filtered. The filtrate was evaporated *in vacuo* to dryness and the residue was extracted with acetone (500 ml). The extract was evaporated *in vacuo* to afford a brown syrup (XIII) (17.5 g) which chromatographed on silica gel (800 g) with cyclohexane-ethyl acetate (7:2 v/v). Yield 9 g $[\alpha]_D^{19} -33.7^\circ$ ($c=1.73$, chloroform). $\nu_{\text{max}}^{\text{film}} \text{cm}^{-1}$: 3500 (OH), 2100 (N_3), 1500 (benzene ring). *Anal.* Found: C, 55.74; H, 5.96; N, 14.12. Calcd. for $\text{C}_{13}\text{H}_{17}\text{O}_4\text{N}_3$: C, 55.91; H, 6.14; N, 15.06%.

Methyl 2-azido-3,4-di-O-benzyl-2-deoxy-L-xylopyranoside (XIV). Powdered potassium hydroxide (25 g) was added to a solution of XIII (8.7 g) in benzyl chloride (50 g). The mixture was heated at 80°~90°C for 4 hr under vigorous stirring. After the mixture was cooled, it was poured into water and extracted with ether (500 ml). The extract was washed with water, dried (Na_2SO_4) and evaporated *in vacuo* (finally below 1 mmHg) to give a pale yellow syrup (11.6 g). The syrup was chromatographed on silica gel (500 g) with benzene as eluent. Yield 9.8 g (85%); $[\alpha]_D^{21} +9.7^\circ$ ($c=1.08$, chloroform), $\nu_{\text{max}}^{\text{film}} \text{cm}^{-1}$: 2100 (N_3), 1500 (benzene ring). *Anal.* Found: C, 64.79; H, 6.00; N, 11.36. Calcd. for $\text{C}_{20}\text{H}_{23}\text{O}_4\text{N}_3$: C, 65.03; H, 6.28; N, 11.37%.

2-Azido-3,4-di-O-benzyl-2-deoxy-L-xylopyranose (XV). Aqueous sulfuric acid (4.5 N, 40 ml) was added to a

solution of XIV (4 g) in acetic acid (80 ml). The mixture was heated at 90°C for 30 hr under stirring, poured into water and extracted with ether (400 ml). The extract was washed with aqueous NaHCO_3 and water, dried (Na_2SO_4) and evaporated *in vacuo* to afford a syrup (3.2 g). The syrup was chromatographed on silica gel (200 g) with cyclohexane-ethyl acetate (3:1 v/v) as eluent to give the syrupy XV (1.9 g, 50%). $[\alpha]_D^{23} +12.5^\circ$ ($c=1.36$, CHCl_3 , no mutarotation), $\nu_{\text{max}}^{\text{film}} \text{cm}^{-1}$: 3400 (OH), 2100 (N_3), 1500 (benzene ring). *Anal.* Found: C, 63.91; H, 5.71; N, 11.80. Calcd. for $\text{C}_{19}\text{H}_{21}\text{O}_4\text{H}_3$: C, 64.21; H, 5.96; N, 11.82%.

2-Amino-2-deoxy- α -L-xylose hydrochloride (L-xylosamine hydrochloride, XVI). A solution of XV (300 mg) in a mixture of *p*-dioxane (25 ml), water (10 ml) and concentrated hydrochloric acid (0.5 ml) was stirred in hydrogen atmosphere in the presence of palladium on carbon (10%) until the absorption of hydrogen stopped. After filtration, the filtrate was evaporated *in vacuo* to give a brown syrup which essentially showed one spot on t.l.c. (Avicel) with *n*-propanol-pyridine-acetic acid-water (15:10:3:10 v/v) as developer. The syrupy XVI was treated with charcoal in methanol and evaporated *in vacuo*. The residual syrup was allowed to stand at room temperature for several days to crystallize. Yield 30 mg (20%) mp 160~162°C (decomposition) $[\alpha]_D^{19} -63.9^\circ$ (5 min) $\rightarrow -46.3^\circ$ (24 hr) ($c=0.58$, water). [D-enantiomer, mp 165~167°C (dec.), $[\alpha]_D^{31} +40^\circ$ (water, final);¹⁰ mp 168~170°C (dec.), $[\alpha]_D^{22} +45^\circ$ (water, 24 hr).¹¹] *Anal.* Found: C, 32.19; H, 6.35; N, 7.47. Calcd. for $\text{C}_5\text{H}_{12}\text{O}_4\text{NCl}$: C, 32.36; H, 6.52, N, 7.55%.

Oxidation of XV with methyl sulfoxide and acetic anhydride. Acetic anhydride (8 ml) was added to a solution of XV (1 g) in methyl sulfoxide (12 ml). The mixture was kept at room temperature for 3 days and poured into water. Water was decanted from a resulting syrupy product. The syrupy product was washed with water several times and extracted with ether (100 ml). The extract was dried (Na_2SO_4) and evaporated *in vacuo* to afford a yellow syrup (950 mg) which reveals inseparable three spots on t.l.c. with benzene-ethyl acetate (15:1 v/v) as developer. This mixture was roughly divided into two fractions by column chromatography with benzene-ether (20:1) as eluent. Both fractions had absorptions at 1730~1740 cm^{-1} (C=O) and 2100 cm^{-1} (N_3). The fast-moving fraction (380 mg) had an IR absorption at 1635 cm^{-1} due to a double bond conjugated to the carbonyl group and gave a positive permanganate test. This fraction was dissolved in aqueous *p*-dioxane (75%) and reduced catalytically with palladium on carbon (10%) in the presence of hydrochloric acid to afford several products. One product was found to have the same *Rf* value as that of authentic 3-deoxy-polyoxamic

acid on t.l.c. (Avicel) with *n*-propanol-pyridine-acetic acid-water (15:10:3:10 v/v) as developer. The slowly-moving fraction (270 mg) had no absorption in the region of 1600~1700 cm⁻¹ and did not give a positive permanganate test. Reduction of this fraction also gave several products, one of which had the same *R_f* value as that of authentic polyoxamic acid on t.l.c. (Avicel) with the developing system described above.

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