[Chem. Pharm. Bull.
11 (12) 1569 ~ 1575]

UDC 547.538.2.07 : 547.435

243. **Tadahiro Iwashige, Motoji Asai, and Issei Iwai :** Studies on Acetylenic Compounds. XXXVI. Total Synthesis of Ethyl 3-Amino-3-deoxy-β-DL-arabinofuranoside.[*1]

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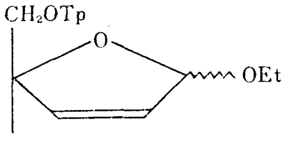
Recently, much attention has been evoked to aminosugars, mainly as 3-aminohexose and 3-aminopentose, because of being important components of several antibiotics.

3-Amino-3-deoxy-D-glucose of kanamycin,[1] 3,6-diamino-3,6-dideoxy-D-glucose of neomycin,[2] 3,6-dideoxy-3-dimethylamino-D-glucose (mycaminose) of magnamycin,[3,4] 3,4,6-trideoxy-3-dimethylamino-D-xylohexose (desosamine)[5~9] of several macrolide antibiotics and also some other aminosugars are known as 3-aminohexose.

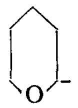
Furthermore, 3-amino-3-deoxy-D-ribose was found to be the component of puromycin.[10] Baker, *et al.*[11,12] has converted 3-amino-3-deoxy-D-arabinose to 3-amino-3-deoxy-D-ribose and, totally synthesized puromycin.

As previously reported,[13] DL-ribose was synthesized stereospecifically from the 2-ethoxy-5-(2′-tetrahydropyranyloxy)methyl-2,5-dihydrofuran (I), which was prepared by the catalytic hydrogenation of DL-1,1-diethoxy-5-(2′-tetrahydropyranyloxy)-2-pentyn-4-ol.



I

Tp =



However, the configuration of C_2-ethoxy and C_5-(2′-tetrahydropyranyloxy) groups was not established and it was tentatively considered that I would be a mixture of *cis* and *trans* isomers.

This report describes the synthesis of ethyl 3-amino-3-deoxy-β-DL-arabinofuranoside (IXDL), following the route shown in Chart 1.

Generally, the epoxidation of I may be carried out with perbenzoic acid or hypochlorous acid, followed by alkaline treatment. An attempted epoxidation of I with perbenzoic acid failed to give an expected product. Therefore, this method was abandoned. Then, hypochlorous acid addition was undertaken, employing calcium hypochlorite under carbon dioxide gas introduction to avoid an acidic condition which causes the acetal bond cleavage. Small portions of calcium hypochlorite was added to the stirred aqueous dioxane solution of I, checking with potassium iodide starch test paper before each addition, to avoid the presence of excess calcium hypochlorite. An oily crude product of chlorohydrin derivative (II), was subjected to next procedure without

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[*1] Part XXXV. I. Iwai, T. Hiraoka : This Bulletin, **11**, 1564 (1963).

[*2] Nishi-shinagawa, Shinagawa-ku, Tokyo (岩重忠博, 浅井素次, 岩井一成).

1) R.U. Lemieux, *et al.* : J. Am. Chem. Soc., **80**, 4741 (1958).
2) K.L. Rinehart, P.W.K. Woo : *Ibid.*, **80**, 6463 (1958).
3) F.A. Hochstein, K. Murai : *Ibid.*, **76**, 5080 (1954).
4) A.B. Foster, T.D. Inch, J. Lehmann, M. Stacey, J.M. Webber : *Chem. & Ind.* (London), **1962**, 142.
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7) H. Brockmann : Angew. Chem., **65**, 257 (1953).
8) C. Djerassi, J.L. Zderic : J. Am. Chem. Soc., 78, 6390 (1956).
9) W. Hofheinz, H. Grisebach : Tetrahedron Letters, No. 9, 377 (1962).
10) B.L. Hutchings, C.W. Waller, P. W. Eryth, J.H. Williams : J. Am. Chem. Soc., **75**, 2025 (1953).
11) B.R. Baker, R.E. Schaub, J.H. Williams : *Ibid.*, **77**, 7 (1955).
12) B.R. Baker, R.E. Schaub, J.P. Joseph, J.H. Williams : *Ibid.*, **77**, 12 (1955).
13) I. Iwai, T. Iwashige, M. Asai, K. Tomita, T. Hiraoka, J. Ide : This Bulletin, **11**, 188 (1963).

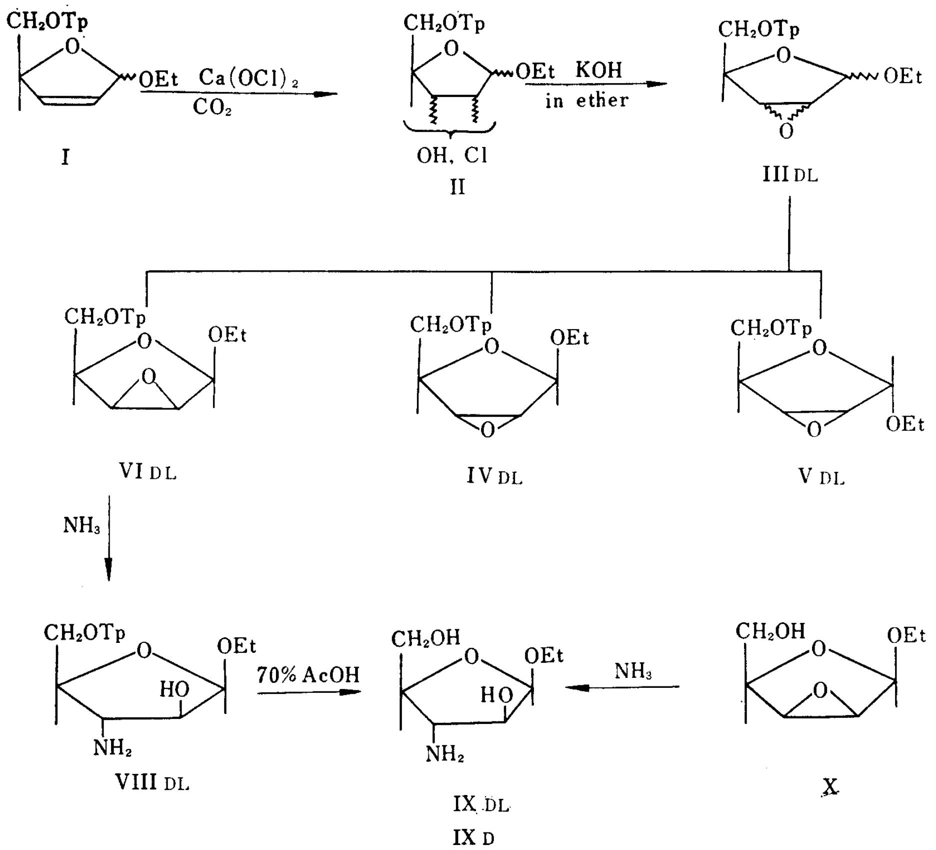
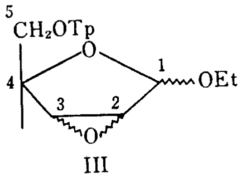


Chart 1.

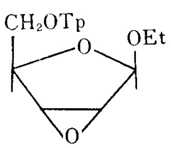
purification, since it tended to decompose on distillation. The ethereal solution of II was shaken with powdered potassium hydroxide to give a viscous oil, b.p.$_{4\times 10^{-5}}$ 105~110°, which was analyzed for ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-DL-pentofuranoside (III DL).



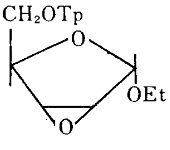
III

Ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydropentofuranoside (III) theoretically requires four isomers for each optical series, due to the configuration of C_{2-3} epoxide ring and C_1-anomeric ethoxy group.

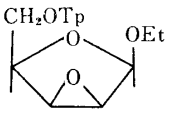
Namely, ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-β-D-ribofuranoside (IV D), ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-α-D-ribofuranoside (V D), ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-β-D-lyxofuranoside (VI D), and ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-α-D-lyxofuranoside (VII D) exist for D-series.



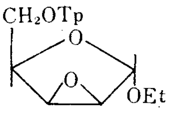
IV D



V D



VI D



VII D

Therefore, some of these racemic isomers or all of them are expected to form on the epoxidation of C_{3-4} double bond of I.

Product, III DL was checked with gaschromatography,[14] using (IV D), (V D), (VI D), (VII D) as control samples, which were prepared from dihydropyran and ethyl 2,3-anhydro-

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[14] M. Horiguchi, N. Higosaki, T. Iwashige, I. Iwai : This Bulletin, **11**, 1056 (1963).

β-D-ribofuranoside, ethyl 2,3-anhydro-α-D-ribofuranoside, ethyl 2,3-anhydro-β-D-lyxofuranoside, ethyl 2,3-anhydro-α-D-lyxofuranoside, respectively. These four furanosides have been prepared according to Baker[11,15] and Percival's[16] procedures.

The gaschromatographic results of IIIDL are shown in Fig. 1 and Table I.

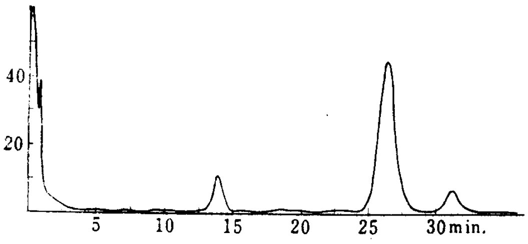


Fig. 1. Gas Chromatogram of IIIDL obtained in first experiment

Column : 1% polyneopentylglycol succinate on 80~100 mesh Chromosorb-W.
Column length : 6 mm. × 2 m.
Column temp. : 125°
Carrier gas : Argon
Argon flow rate : 67.5 ml. /min.
Detector : ^3H

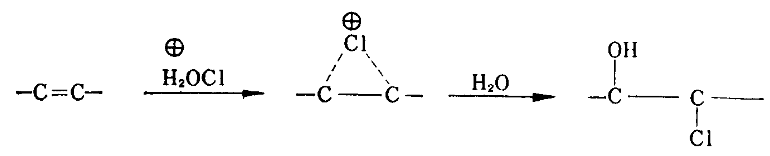
Table I. Area Ratio[a] of Three Components (relative to VIDL) obtained in Each Gas Chromatography of IIIDL

Exp. No.	(IVDL) (13.8)	(VIDL) (26.3)	(VDL) (31.2)[b]
1	0.20	1.0	0.18
2	0.45	1.0	0.23
3	0.19	1.0	0.09

a) Determined by weighing method
b) Retention time (min.)

The discussion on these data will be provided in the way described below.

It is generally accepted as possible mechanism[17] that hypochlorous acid addition to double bond proceeds through bridged chloronium cation to give a chlorohydrin derivative.



Regarding I to be a mixture of DL-*cis*-2-ethoxy-5-(2′-tetrahydropyranyloxy) methyl-2,5-dihydrofuran (XI) and its *trans* isomer (XII), XIII, XIV from XI and XV, XVI from XII can be expected as all possible bridged chloronium cations.

Although hydrolysis of each bridged chloronium cation might give two kinds of *trans* chlorohydrin derivatives, the treatment of these two chlorohydrins with alkali should give the same epoxide and consequently each chloronium cation would afford an epoxide ring with opposite configuration.

Considering the steric effect and neighbouring participation of C_1-anomeric ethoxy group, XIII would be more favored over XIV. Consequently, epoxide VIDL must be predominantly afforded, comparing with IVDL. However, in case of *trans* isomer, XII, the appreciable steric effect would not concern on the bridged chloronium cation formation, but XV would be more favored over XVI, due to the neighbouring participation of C_1-anomeric ethoxy group. Accordingly, VDL is expected to be major product and VIIIDL to be minor, starting from XII.

Actually, the experimental results shown in Fig. 1 and Table I, have proved that VIDL was major product and IVDL, VDL were minor ones, but no VIIIDL was found in all

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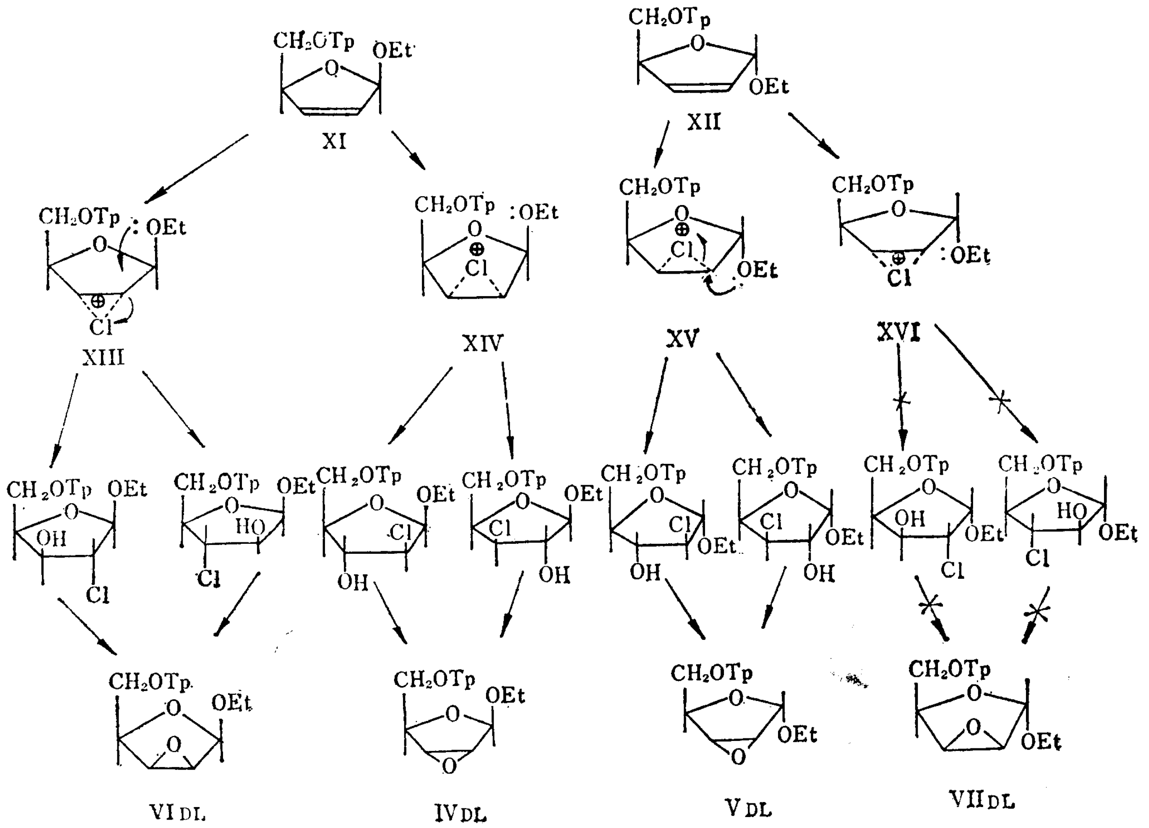
15) C.D. Anderson, L. Goodman, B.R. Baker : J. Am. Chem. Soc., **80**, 5247 (1958).
16) J.M. Anderson, E. Percival : J. Chem. Soc., **1956**, 819.
17) E.S. Gould : "Mechanism and Structure in Organic Chemistry," Henry Holt & Co., Inc., (1959), 525.



cases. It was also concluded from these results, that DL-*cis*-2-ethoxy-5-(2′-tetrahydropyranyloxy)methyl-2,5-dihydrofuran (XI) was predominantly formed and the other possible *trans* isomer (XII) was found only as minor component on the catalytic hydrogenation of DL-1,1-diethoxy-5-(2′-tetrahydropyranyloxy)-2-pentyn-4-ol. However, the reasonable interpretation for the predominant formation of XI has not been forwarded.

Contrary to our results, Hawkins and Bannard[18] reported that they predominantly obtained the *trans* epoxide by the action of alkali on 1-ethoxycyclohexene-2-bromohydrin. They did not stress much this point. Further discussion remains pending that whether the reaction goes through different mechanism, or controlling by additional factors, between unsaturated five and six membered rings.

Then IIIDL was chromatographically separated on silica gel, eluting with benzene initially and then with benzene-chloroform (4:1) after IVDL had been eluted. Each fraction was checked by gas and thin layer chromatographies. Finally, IVDL, VDL, and VIDL could be separated. The infrared spectrum of each isomer was identical with that of the corresponding isomer for D-series, IVD, VD, VID, as shown in Figs. 2, 3, and 4.

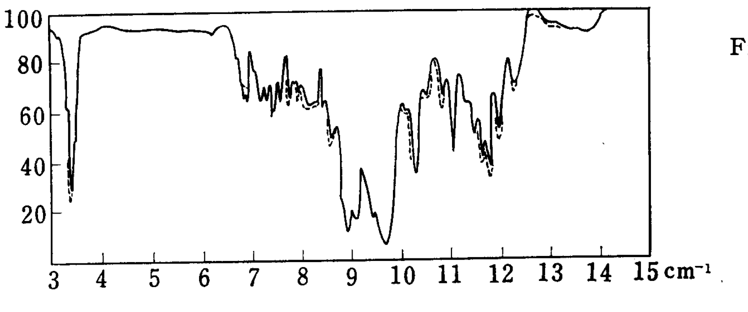


Fig. 2. Infrared Absorption Spectra (in $CHCl_3$)

—— Ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-β-DL-ribofuranoside (IVDL)

------ Ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-β-D-ribofuranoside (IVD)

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[18] R.A.B. Bannard, L.R. Hawkins: Can. J. Chem., **36**, 1241 (1958).

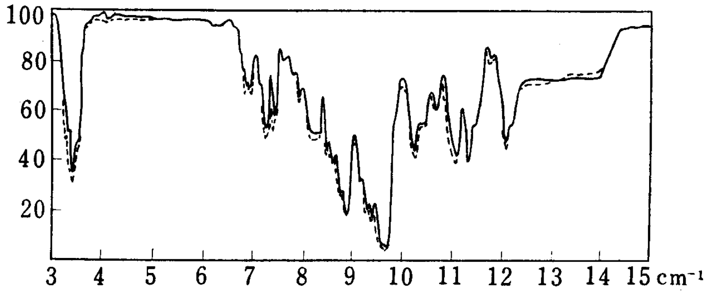

Fig. 3. Infrared Absorption Spectra (in $CHCl_3$)

—— Ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-α-D-ribofuranoside (VD)

------ Ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-α-DL-ribofuranoside (VDL)

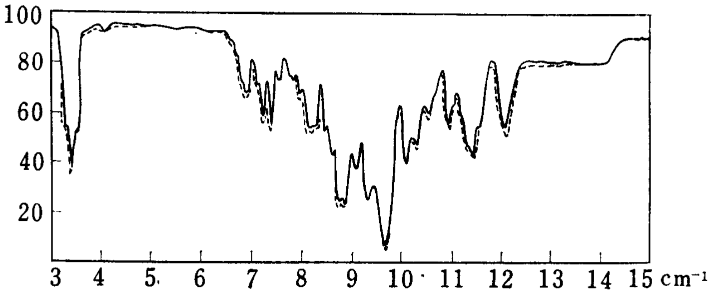

Fig. 4. Infrared Absorption Spectra (in $CHCl_3$)

—— Ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-β-D-lyxofuranoside (VID)

------ Ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-β-DL-lyxofuranoside (VIDL)

The major component VIDL was treated with alcoholic ammonia to give an oil, b.p.$_{2\times10^{-4}}$ 110~120° (bath temp.), which was analyzed for ethyl 3-amino-3-deoxy-5-O-(2-tetrahydropyranyl)-β-DL-arabinofuranoside (VIIIDL). Since the preferential attack of nucleophilic reagent at C_3 is generally known for the epoxide ring of 2,3-anhydropentofuranoside,[11,16,19,20] VIIIDL was treated with 70% acetic acid to give ethyl 3-amino-3-deoxy-β-DL-arabinofuranoside (IXDL), without confirming whether VIIIDL was contaminated with another possible 2-amino derivative. An oil, b.p.$_{0.2}$ 125~130° (bath temp.) which was analysed for IXDL and partially solidified on standing, was initially obtained. However, it was found to be probably contaminated with 2-amino derivative, since thin layer chromatography (TLC) showed small spot Rf=0.47~0.50 besides Rf=0.37~0.39 which was due to IXDL, using ethyl 3-amino-3-deoxy-β-D-arabinofuranoside IXD as the control sample. Recrystallization from benzene-chloroform gave the crystal m.p. 85~96° which showed the superimposable infrared spectrum with that of IXD as shown in Fig. 5 and single spot, Rf=0.37~0.39 by TLC.

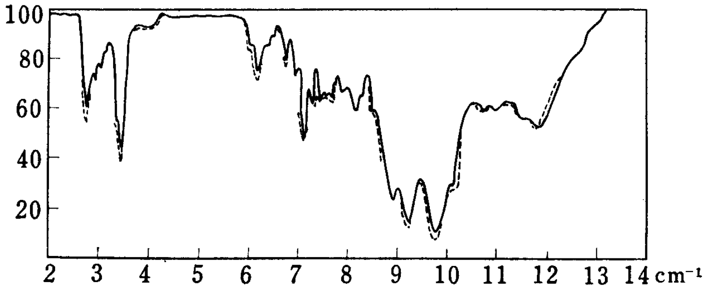

Fig. 5. Infrared Absorption Spectra (in $CHCl_3$)

—— Ethyl 3-amino-3-deoxy-β-DL-arabinofuranoside (IXDL)

------ Ethyl 3-amino-3-deoxy-β-D-arabinofuranoside (IXD)

Consequently, the total synthesis of ethyl 3-amino-3-deoxy-β-DL-arabinofuranoside (IXDL) from 2-ethoxy-5-(2′-tetrahydropyranyloxy)methyl-2,5-dihydrofuran (I) has been achieved.

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19) J. Davoll, B. Lythgoe, S. Trippet: J. Chem. Soc., **1951**, 2230.

20) R.U. Lemieux, R.K, Kullnig, R.Y. Moir: J. Am. Chem. Soc., **80**, 2237 (1958).

Experimental

Ethyl 5-O-(2′-Tetrahydropyranyl)-2,3-anhydro-DL-pentofuranoside (IIIDL)——To a stirred solution of 90 g. of 2-ethoxy-5-(2′-tetrahydropyranyloxy)methyl-2,5-dihydrofuran (I) in 1 L. of 50% aqueous dioxane, cooled at 3 to 7° was added 62 g. of calcium hypochlorite (60% purity) with 2~3 g. portions, under continuous carbon dioxide gas introduction. Each addition was undertaken by negative iodine-starch test of the reaction mixture and period of 30 hr. was required for the completion. The dioxane layer was separated by salting out with NaCl and the aqueous layer was extracted with Et_2O four times. Combined organic solution was washed with saturated aqueous NaCl and dried over $MgSO_4$, then evaporated at below 40° under reduced pressure. A solution of about 120 g. of residue in 500 ml. of anhyd. Et_2O was added slowly into 100 g. of powdered KOH suspended in 500 ml. of anhyd. Et_2O under ice cooling, and shaken for 5 hr. The reaction mixture was filtered through Celite and the filtrate was evaporated. Distillation of the residue gave 45.1 g. of an oil, $b.p_{4\times10^{-5}}$ 105~110°. *Anal.* Calcd. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found : C, 58.79; H, 8.08.

Chromatographic Separation of IIIDL——Twenty grams of IIIDL was chromatographed on 1kg. of silica gel, eluting with benzene initially and then with benzene-$CHCl_3$(4:1), when 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-β-DL-ribofuranoside (IVDL) was almost eluted. Each fraction thus obtained in the order described below was checked by both gas and thin layer chromatographies.

TABLE II.

Fraction No.	Component of Fraction	Yield (g.)	Refractive Index	Rf*3
1	Ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-β-DL-ribofuranoside (IVDL)	2.2	n_D^{16} 1.4655, n_D^{21} 1.4646 (D-isomer, IVD)	0.67~0.69
2	(IVDL)+Ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-β-DL-lyxofuranoside (VIDL)	0.5		
3	(VIDL)	7.4	n_D^{16} 1.4718, n_D^{22} 1.4708 (D-isomer, IVD)	0.50~0.52
4	(VIDL)+Ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-α-DL-ribofuranoside (VDL)	5.95		
5	(VDL)	0.82		0.48~0.50

Ethyl 3-Amino-3-deoxy-β-DL-arabinofuranoside (IXDL)——A solution of 1.4 g. of ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-β-DL-lyxofuranoside (VIDL) in 14 ml. of alcoholic ammonia solution saturated at 0° was heated at 110° in sealed tube for 48 hr. The cooled reaction mixture was concentrated. A viscous oily residue was dissolved in MeOH and evaporated again. The residue obtained was dissolved in H_2O, adsorbed on IRC-50 and eluted with 2 *N* NH_4OH. The combined eluates were concentrated *in vacuo* at room temperature. The distillation of residue gave 1.1 g. of an oil, $b.p_{2\times10^{-4}}$ 110~112° (bath temp.), which was analyzed for ethyl 5-O-(2′-tetrahydropyranyl)-3-amino-3-deoxy-β-DL-arabinofuranoside (VIIIDL) and this oil showed the positive Ninhydrin test. *Anal.* Calcd. for $C_{12}H_{23}O_5N$: C, 55.15; H, 8.87; N, 5.36. Found: C, 55.32; H, 9.06; N, 5.03.

A solution of 0.25 g. of crude previously obtained ethyl 3-amino-3-deoxy-5-O-2′-tetrahydropyranyl-β-DL-arabinofuranoside (VIIIDL) in 2.5 ml. of 70% AcOH was heated at 60° for 3 hr. The reacton mixture was concentrated *in vacuo* below 40°. The residue was dissolved in H_2O, treated with Dowex-1 to remove $^-$OAc. The resultant aqueous solution was adsorbed on IRC-50 to remove a neutral material, then eluted with 2*N* NH_4OH. The combined eluates were concentrated *in vacuo* at room temperature and the residue was dissolved in MeOH, treated with charcoal and concentrated. Distillation of the viscous residue gave 0.12 g. of an oil, $b.p_{0.2}$ 125~130° (bath temp.), which was partially solidified on standing. This partially solidified oil showed the positive Ninhydrin test and two spots, Rf=0.37~0.39 (ethyl 3-amino-3-deoxy-β-DL-arabinofuranoside), Rf=0.47~0.49 (probably due to 2-amino-2-deoxy-derivative) by TLC.*4

Recrystallization from $CHCl_3$-benzene gave a crystalline material, m.p. 85~96°, which showed only one spot, Rf=0.37~0.39 by TLC and the identical IR spectrum with that of ethyl 3-amino-3-deoxy-β-D-arabinofuranoside (IXD) in $CHCl_3$. *Anal.* Calcd. for $C_7H_{15}O_4N$: C, 47.44; H, 8.53; N, 7.91. Found: C, 47.14; H, 8.34; N, 7.83. IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 3600 (OH), 3430, 3360 (NH), 1595 (NH).

Ethyl 3-Amino-3-deoxy-β-D-arabinofuranoside (IXD)——A solution of 2 g. of ethyl 2,3-anhydro-β-D-lyxofuranoside (X) in 20 ml. of alcoholic ammonia solution, saturated at 0°, was heated at 110~120°

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*3 Silica Gel G, Merck. Solvent : benzene-$CHCl_3$-Me_2CO (6:3:1).

*4 Silica Gel G, Merck. Solvent : MeOH-benzene-Me_2CO (2:1:7). Detecting agent : Ninhydrin.

in sealed tube for 48 hr. The cooled red-brown solution was concentrated *in vacuo*. The residue was dissolved in small amount of EtOH and evaporated. The resultant syrupy product was dissolved in small amount of H_2O, adsorbed on IRC-50 and eluted with 2*N* NH_4OH. The combined eluates were concentrated *in vacuo* and the residue was dissolved in MeOH, treated with charcoal. A crude product weighing 2 g. obtained on evaporation of solvent was recrystallized from $CHCl_3$ to give crystals, m.p. 115~116°, which showed Rf=0.37~0.39 by TLC*4 and had $[\alpha]_D^{27.5}$ −127°(1.6% in $CHCl_3$). *Anal.* Calcd. for $C_7H_{15}O_4N$: C, 47.44; H, 8.53; N, 7.91. Found : C, 47.23; H, 8.50; N, 7.95.

Preparation of Ethyl 2,3-Anhydro-β-D-lyxofuranoside (X), Ethyl 2,3-Anhydro-α-D-lyxofuranoside, Ethyl 2,3-anhydro-β-D-ribofuranoside, Ethyl 2,3-Anhydro-α-D-ribofuranoside——As described before, these four furanosides were synthesized following Baker[11,15)] and Percival's[16)] procedures.

Ethyl 2,3-Anhydro-β-D-lyxofuranoside (X)——b.p$_{0.06}$ 100~110°(bath temp.). $[\alpha]_D^{32}$ −77°(3% in H_2O). *Anal.* Calcd. for $C_7H_{12}O_4$: C, 52.49; H, 7.50. Found C, 52.61; H, 7.48..

5-O(2′-Tetrahydropyranyl)derivative (VID): To a solution of 1 g. of X and 5.8 ml. of dihydropyran in 20 ml. of $CHCl_3$, one drop of $POCl_3$ was added. Heat evolution was observed a few minutes later. The reaction mixture was stirred further for 30 min. and washed with 5% $NaHCO_3$, then evaporated *in vacuo* to remove solvent and unreacted dihydropyran after drying over $MgSO_4$. Distillation of the residue gave 1.2 g. of an oil, b.p$_{5\times10^{-4}}$ 110~120°(bath temp.), n_D^{22} 1.4708, $[\alpha]_D^{30}$ −79°(3.4% in $CHCl_3$). *Anal.* Calcd. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found : C, 59.09; H, 8.04.

5-O-Acetyl derivative : A solution of 1.5 g. of X in 2.8 ml. of pyridine and 1.1 ml. of Ac_2O was left at room temperature for 2 days and treated through routine procedure to give 1.6 g. of an oil, b.p$_{3\times10^{-4}}$ 94~100°(bath temp.), $[\alpha]_D^{27}$ −67°(3.5% in $CHCl_3$). *Anal.* Calcd. for $C_9H_{14}O_5$: C, 52.95; H, 6.93. Found : C, 52.93; H, 6.90.

Ethyl 2,3-Anhydro-α-D-lyxofuranoside——m.p. 58~59°, $[\alpha]_D^{29}$ +40.3°(2.1% in H_2O). *Anal.* Calcd. for $C_7H_{12}O_4$: C, 52.49; H, 7.50. Found : C, 52.47; H, 7.45.

5-O-(2′-Tetrahydropyranyl)derivative (VIID) : prepared following the procedure for VID. b.p$_{5\times10^{-4}}$ 110~120°(bath temp.), n_D^{21} 1.4652, $[\alpha]_D^{29}$ +21° (4.2% in $CHCl_3$). *Anal.* Calcd. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found : C, 59.17; H, 8.21.

5-O-Acetyl derivative : prepared following the procedure described above. b.p$_{10^{-4}}$ 75~85° (bath temp.), $[\alpha]_D^{28}$ +44°(6.2% in $CHCl_3$). *Anal.* Calcd. for $C_9H_{14}O_5$: C, 52.95; H, 6.93. Found : C, 53.27; H, 6.91.

Ethyl 2,3-Anhydro-β-D-ribofuranoside——b.p$_{5\times10^{-4}}$ 73~80°(bath temp.). $[\alpha]_D^{29.5}$ −89.5°(3% in H_2O). *Anal.* Calcd. for $C_7H_{12}O_4$: C, 52.49; H, 7.50. Found : C, 52.88; H, 7.63.

5-O-(2′-Tetrahydropyranyl) derivative (IV$_D$): b.p$_{5\times10^{-4}}$ 100~110°(bath temp.), n_D^{21} 1.4646, $[\alpha]_D^{30}$ −99° (4.1% in $CHCl_3$). *Anal.* Calcd. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found : C, 58.89; H, 8.17.

5-O-Acetyl derivative : b.p$_{10^{-4}}$ 45~55°(bath temp.). $[\alpha]_D^{27}$ −108°(3% in $CHCl_3$). *Anal.* Calcd. for $C_9H_{14}O_5$: C, 52.95; H, 6.93. Found : C, 53.27; H, 6.91.

Ethyl 2,3-Anhydro-α-D-ribofuranoside——b.p$_{5\times10^{-4}}$ 100~105°(bath temp.). $[\alpha]_D^{30}$ +13.1°(15.3% in $CHCl_3$), *Anal.* Calcd. for $C_7H_{12}O_4$: C, 52.49; H, 7.50. Found : C, 53.18; H, 7.64.

5-O-(2′-Tetrahydropyranyl)derivative (VD): b.p$_{5\times10^{-4}}$ 115~125°(bath temp.), n_D^{21} 1.4698, $[\alpha]_D^{31}$ −14.3° (15% in $CHCl_3$). *Anal.* Calcd. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found : C, 59.19; H. 8.06.

5-O-Acetyl derivative : b.p$_{10^{-4}}$ 85~90°(bath temp.), $[\alpha]_D^{27}$ −18.4°(14.2% in $CHCl_3$). *Anal.* Calcd. for $C_9H_{14}O_5$: C, 52.95; H, 6.93. Found : C, 53.15; H, 6.71.

The authors express their deep gratitudes to Dr. M. Matsui, Director of this laboratory and Dr. B. Shimizu, the chief research chemist, for their warmful encouragements throughout the course of this investigation. They are also greatly indebted to Messrs, K. Iwase and M. Ito for their technical corporation. The measurement of infrared and gas chromatography was carried out by Messrs. M. Horiguchi, H. Higuchi, N. Higosaki, T. Fujimura, Miss N. Sawamoto and microanalyses were performed by Dr. T. Onoe, Messrs. K. Ono, H. Nagashima and Misses. K. Saito and N. Gonda.

Summary

Ethyl 5-O-(2′-tetrahydropyranyl)-2,3-anhydro-β-DL-lyxofuranoside(VIDL)was predominantly formed by the action of alkali on a chlorohydrin derivative, which was prepared by hypochlorous acid addition of 2′-ethoxy-5-(2′-tetrahydropyranyloxy)methyl-2,5-dihydrofuran (I). Then, ethyl 3-amino-3-deoxy-β-DL-arabinofuranoside (IXDL) was synthesized from VIDL.

(Received May 28, 1963)