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Total Syntheses of Carbohydrates. III. DL-Glyceraldehyde and 2-Deoxy-DL-*erythro*-pentose

Kosuke MIMAKI, Michihiko MASUNARI, Gen NAKAMINAMI, and Masazumi NAKAGAWA*

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka

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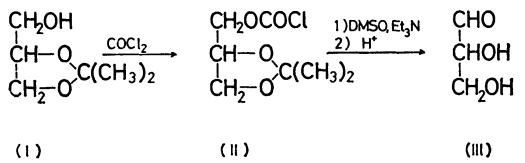
The synthesis of DL-glyceraldehyde (III) by the Barton's oxidation of DL-isopropylideneglycerol (I) was described. 2-Deoxy-DL-*erythro*-pentose (IX) (2-deoxy-DL-ribose) has been synthesized by the Barton's oxidation of 2-deoxy-3,4-*O*-isopropylidene-5-*O*-(tetrahydro-2-pyranyl)-DL-*erythro*-pentitol (VIII) and by the hydroboration of DL-*erythro*-4-pentyn-1,2,3-triol (XI) followed by hydrogen peroxide oxidation. The latter method gave crystalline 2-deoxy-DL-*erythro*-pentose (IX) in a reasonable yield.

In the previous papers, we have reported the syntheses of dihydroxyacetone,[1] DL-*glycero*-tetrulose,[1] DL-threose[2] and DL-erythrose[2] starting from simple acetylenic compounds. Selective synthesis of *cis*- and *trans*-ethylenic compounds followed by stereospecific hydroxylation of ethylenic linkage and introduction of carbonyl function played important roles in the syntheses of these carbohydrates. In the present paper, we wish to report a new syntheses of DL-glyceraldehyde (III) and the syntheses of 2-deoxy-DL-*erythro*-pentose (IX) according to two different routes.

The Pfitzner-Moffatt reagent[3] has been proved to be adequate for the conversion of primary alcohol to aldehyde. However, disadvantage of application of this reagent[4] or the dimethylsulfoxide-acetic anhydride reagent[5] for carbohydrate synthesis has been pointed out by several authors. We have carried out the synthesis of DL-glyceraldehyde (III) by means of the Barton's oxidation[6] proving the usefulness of this procedure for carbohydrate synthesis. As is illustrated in Scheme 1, DL-isopropylideneglycerol (I) in dry ether was treated with phosgene in the presence of quinoline to give chloroformate (II) in a good yield. Purification of chloroformate (II) was achieved by a distillation under reduced pressure. However, the crude II could be used in the subsequent reaction without difficulty. Crude chlorofomate (II) was mixed with dimethyl sulfoxide resulting in evolution of carbon dioxide. After treatment with triethylamine, the protective group was hydrolyzed by means of ion-exchange resin. DL-Glyceralehyde (III) was obtained as syrupy liquid, and gave a single spot on tlc which corresponds exactly with that of an authentic specimen. The syrupy glyceradehyde (III) partly crystallized on standing. 2,4-Dinitrophenylhydrazone of III was obtained in a yield of 33% based on DL-isopropylideneglycerol (I).



(I) (II) (III)

Scheme 1. Synthesis of DL-glyceraldehyde (III). DMSO=dimethyl sulfoxide

The successful result of the Barton's oxidation prompted the present authors to the synthesis of 2-deoxy-DL-*erythro*-pentose (IX) employing the same oxidation reaction.

The total syntheses of 2-deoxy-*erythro*-pentose (IX) have been reported by Fraser and Raphael[7] and Weygand and Leube.[8] In the former case, the yield of the pentose was found to be unsatisfactory, however, anilide of 2-deoxy-*erythro*-pentose (IX) was obtained in an overall yield of 2.5% in the latter case using commercially available 1-methoxy-1-buten-3-yne as starting meterial.

The reaction sequence we have employed was shown in Scheme 2.

The reaction of lithium acetylide of tetrahydropyranyl ether derivative of propargyl alcohol (IV) in refluxing liquid ammonia with ethylene oxide gave

* The author to whom inquiries should be addressed.

1) T. Ando, S. Shioi, and M. Nakagawa, This Bulletin, **45**, 2611 (1972).

2) K. Sonogashira and M. Nakagawa, *ibid.*, **45**, 2616 (1972).

3) K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 5661, 5670 (1965).

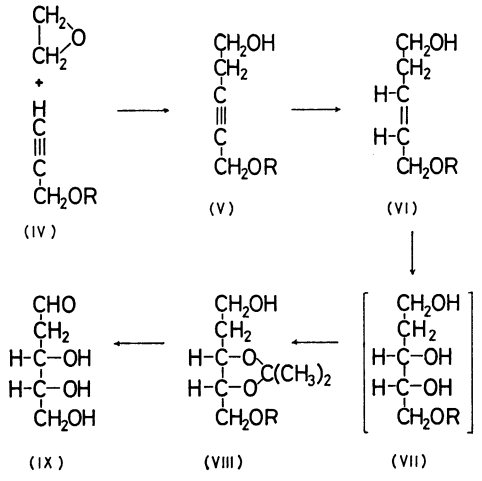
4) D. Horton, M. Nakadate, and J. M. J. Tronchet, *Carbohyd. Res.*, **7**, 56 (1968).

5) J. L. Godman and D. Horton, *ibid.*, **6**, 229 (1968).

6) D. H. R. Barton, B. J. Garner, and R. H. Wightman, *J. Chem. Soc.*, **1964**, 1855.

7) M. M. Fraser and R. A. Raphael, *ibid.*, **1955**, 4280.

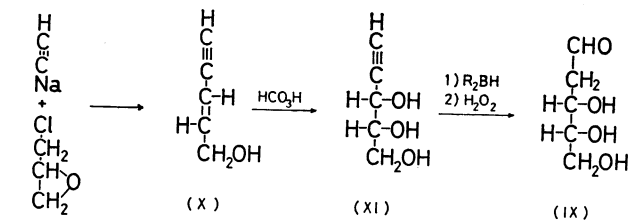
8) F. Weygand and H. Leube, *Chem. Ber.*, **89**, 1914 (1956).



Scheme 2. Synthesis of 2-deoxy-DL-*erythro*-pentose (IX).
R=tetrahydropyranyl
The formulae of D-isomers are shown for brevity.

C_5-acetylenic compound (V) in a high yield. A half-reduction of V by means of Lindlar catalyst[9] afforded C_5-*cis*-ethylenic compound (VI). VI was treated with potassium permanganate to cause *cis*-hydroxylation of the *cis*-ethylenic bond. 3,4-*erythro*-Compound (VII) was obtained as a viscous syrup. Syrupy VII, which was proved to be fairly homogeneous by tlc, was subjected to the following reaction without purification. A difficulty was encountered in the conversion of VII to the corresponding acetonide (VIII). The reaction of VII with acetone in the presence of anhydrous cupric sulfate was followed by IR spectroscopy and tlc. The change of IR spectra indicated that the cleavage of tetrahydropyranyl group occurred accompanying an anomalous increase in the amount of dimethyldioxolane ring on heating the mixture under reflux. Therefore, the reaction was carried out at room temperature, and the reaction was quenched as soon as the spot of VII in tlc disappeared. Chromatographic purification of the reaction product on alumina gave crude isopropylidene derivative (VIII) in a low yield. The Barton's oxidation[6] of the crude VIII followed by acid hydrolysis of the protective groups resulted in a syrupy product, which gave a spot corresponding to that of authentic 2-deoxy-D-*erythro*-pentose. The crude 2-deoxy-DL-*etythro*-pentose (IX) thus obtained gave crystalline anilide in a low yield. The preparation of 2-deoxy-DL-*erythro*-pentose (IX) according to the reaction sequence indicated in Scheme 2 resulted in a rather unsatisfactory consequence. However, the usefulness of the Barton's oxidation in carbohydrate chemistry seems to remain for further investigation.

Preparation of aldehyde by addition of bis(1,2-dimethylpropyl)borane to terminal ethynyl group followed by oxidation with hydrogen peroxide has been reported by Brown and Zweifel.[10] Application of this method to a poly-ol having an ethynyl group is a conceivable route of synthesis of 2-deoxyaldose. DL-*erythro*-4-Pentyn-1,2,3-triol (XI),[11] a precursor for the synthesis of DL-*erythro*-pentose (IX), is a known compound prepared by *trans*-hydroxylation of *trans*-2-penten-4-yn-1-ol (X)[12] by means of performic acid. According to the reaction sequence illustrated in Scheme 3, the triol (XI) was treated with an excess of bis(1,2-dimethylpropyl)borane and the reaction product was oxidized with hydrogen peroxide under careful addition of 1N sodium hydroxide solution to neutralize the resulting boric acid, and to keep the pH of medium at 7.0—7.5. The control of pH is essential in this reaction. An appreciable decrease in the yield of IX was observed when the pH of medium increased to *ca.* 9. The reaction mixture was mixed with sodium hydrogen sulfite solution, and then deionized with ion-exchange resin. The syrup obtained by removing boric acid as methyl ester was treated with aniline according to the usual manner. The anilide thus obtained was found to be identical with that of an authentic D-IX and that of DL-IX which was prepared by another synthetic route.[13] The IR spectra of anilide derived from DL-IX and an authentic D-IX are recorded in Fig. 1. The yield of anilide of IX on the basis of ethynyl compound (XI) was found to be 20%, and the overall yield from epichlorohydrin was 3.8%. The free pentose (IX) obtained from anilide crystallized completely on seeding with a piece of crystal of an authentic D-isomer. The elemental analysis and the comparison of tlc with that of an authentic D-IX indicate that the crystals are 2-deoxy-*erythro*- pentose (IX). The pentose (IX) showed no optical activity over a wide range of wavelength indicating the crystallization of DL-isomer. This is the



Scheme 3. Another synthesis of 2-deoxy-DL-*erythro*-pentose (IX).
R=$(CH_3)_2CH$–$\underset{CH_3}{CH}$–
The formulae of D-isomers are shown for brevity.

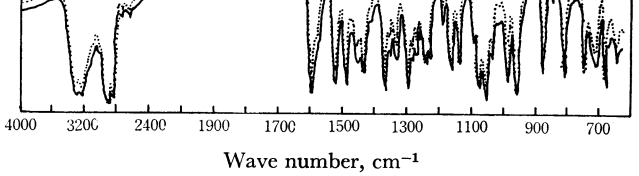


Fig. 1. IR spectra of anilide of DL-IX (——) and anilide of an authentic D-IX (·····), (Nujol mull).

9) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).
10) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **81**, 1512 (1959); **83**, 3834 (1961).
11) R. A. Raphael, *J. Chem. Soc.*, **1949**, S 44.
12) L. J. Haynes, I. M. Heilbron, E. R. H. Jones, and F. Sondheimer, *ibid.*, **1947**, 1583.
13) G. Nakaminami, S. Shioi, Y. Sugiyama, S. Isemura, M. Shibuya, and M. Nakagawa, This Bulletin, **45**, 2624 (1972).

first instance of crystalline 2-deoxy-DL-*erythro*-pentose (IX).

After completion of this study, an independent paper on the application of hydroboration for the synthesis of α,β-ethylenic aldose derivatives was published.[14]

Experimental

Silica Gel G (E. Merck, Darmstadt, Germany) was used for tlc. Anisaldehyde–sulfuric acid–acetic acid–ethanol[15a] (A), concentrated sulfuric acid[15b] (B) and diphenylamine–sulfuric acid–acetic acid[16] (C) were used as detection reagents. In the case of reagent (C), the splayed tlc plate was covered with another glass plate and baked at 90—100°C to develop the color. IR spectroscopy was performed with a Hitachi EPI-2 or a Japan Spectroscopic DS-402G Spectrophotometer. NMR spectra were obtained on Varian A-60 Spectrometer operated at 60 MHz using TMS as internal standard. All the melting points are uncorrected.

*1-O-Chloroformyl-2,3-O-isopropylidene-*DL*-glycerol (II).* A solution of DL-isopropylideneglycerol[17] (I, 13.2 g, 0.1 mol) and quinoline (12.9 g, 0.1 mol) in anhydrous ether (150 m*l*) was strongly chilled on an ice-salt bath. Phosgene passed through linseed oil and concentrated sulfuric acid was introduced for 2 hr into the chilled solution under stirring. Further stirring was continued for 30 min under cooling, and then for 2 hr at room temperature. The reaction mixture was filtered to remove quinoline hydrochloride with the aid of slight excess air pressure avoiding atmospheric moisture. Evaporation of the filtrate under reduced pressure yielded viscous light yellow liquid [15.6 g, 80%, IR (neat): 1784 (Cl–C=O), 1383, 1375, 842 (dimethyl dioxolane) cm^{-1}]. The crude chloroformate (II) could be used without purification in the subsequent reaction. Crude II turned to brown in a few days on standing at room temperature. A vacuum distillation of the crude material afforded pure II as colorless liquid, bp 75°C/7 mmHg, n_D^{25} 1.4381, NMR (CCl_4): δ 1.32 (3H, s) CH_3; δ 1.39 (3H, s) CH_3.

Found: C, 43.93; H, 5.75; Cl, 17.99%. Calcd for $C_7H_{11}O_4Cl$: C, 43.20; H, 5.70; Cl, 18.22%.

DL-*Glyceraldehyde (III).* Dimethyl sulfoxide (5 m*l*) was added to chloroformate (II, 973 mg, 5 mmol) at 10—15°C under vigorous evolution of carbon dioxide. After 2 min, the cooling bath was removed, and the mixture was stirred for 15 min at room temperature (>20°C). The mixture was then chilled on an ice-bath and mixed with triethylamine (607 mg, 6 mmol). After the mixture had been stirred for 3 min at the temperature, stirring was continued for 20 min at room temperature (>20°C). Triethylammonium chloride deposited was removed by filtration. The filtrate was mixed with a cation exchange resin [Amberlite IR-200 (H^+) in water (10 m*l*)]. After the mixture had been stirred for 2 hr under ice cooling, an anion exchange resin [Dowex-3 (OH^-)] was added to remove chloride ion. The resins were removed by filtration and washed with water. The combined filtrate and washing, which gave negative silver nitrate and Beilstein tests, were concentrated under reduced pressure at a temperature below 35°C. After most of the water had been distilled off, remaining dimethyl sulfoxide was removed under high vacuum at the same temperature. The resulting syrup reduced strongly the Tollens' and the Fehling's solutions. The absorption arising from dimethyldioxolane ring completely disappeared in the IR spectrum of the syrupy material. The syrup gave one spot (R_f 0.36) on tlc (solvent: acetone; detection reagent: A or B), and the spot of isomeric dihydroxyacetone (R_f 0.64) or another spot could not be observed. An acetone solution of the syrup was placed for a long time in a refrigerator, resulting in deposition of a small amount of colorless rods, mp 127—135°C [lit, mp 138°C,[18] mp 142.5°C[19]]. The colorless crystals gave identical tlc with that of an authentic specimen. An acetone solution of syrupy III obtained by another run gave a small amount of colorless powder. The substance showed no definite melting point, but underwent color change to brown at *ca.* 200°C. However, tlc and IR spectrum of the colorless solid were found to be identical with those of an authentic specimen (*Cf.*, Fig. 2). It has been reported that the melting point of DL-glyceraldehyde (III) varies widely depending on the rate of heating and the method of measurement.[20] Our observation seems to be related with this phenomenon.

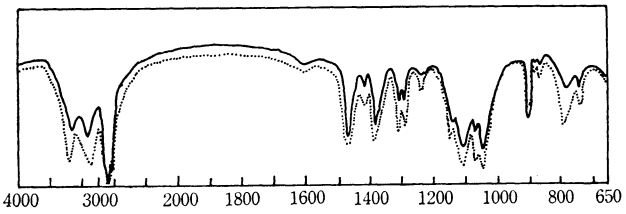


Fig. 2. IR spectra of DL-glyceraldehyde [mp *ca.* 200°C (decomp.)] (——) and an authentic DL-glyceraldehyde (·····), (Nujol mull).

2,4-Dinitrophenylhydrazone of DL*-Glyceraldehyde.* Syrupy DL-glyceraldehyde (III, 180 mg) was converted to the 2,4-dinitrophenylhydrazone (105.5 mg, 33% based on II) according to the reported method.[21] The hydrazone was recrystallized from ethyl acetate to give pure material, mp 169—169.5°C [lit,[21] mp 170°C]. 2,4-Dinitrophenylhydrazone thus prepared showed no depression of melting point on admixture with that of an authentic DL-glyceraldehyde, and the IR spectrum was superimposable with that of authentic specimen.

Found: C, 40.06; H, 3.85; N, 20.72%. Calcd for $C_9H_{10}O_6N_4$: C, 40.00; H, 3.73; N, 20.74%.

5-(Tetrahydro-2-pyranyloxy)-3-pentyn-1-ol (V). A solution of tetrahydropyranyl ether of propargyl alcohol[22] (IV, 60 g, 0.429 mol) in ether (36 m*l*) was added over a period of 1 hr to a stirred solution of lithium amide (prepared from lithium, 0.6 g, 0.87 g-atom) in liquid ammonia (600 m*l*). After the mixture had been stirred for 2 hr, ethylene oxide (60 m*l*, 1.2 mol) was added in a portion. The mixture was refluxed for 14.5 hr at a temperature of −26——30°C using a cold-finger reflux condenser containing dry ice-ethanol. After addition of a concentrated aqueous ammonia solution (6 m*l*), the ammonia was allowed to evaporate. The residue was mixed with water and extracted with ether. The extract

14) D. Horton, J. B. Hughes, and J. M. J. Tronchet, *Chem. Commun.*, **1965**, 481.

15) K. Randerath, translated by D. D. Libman, "Thin-layer Chromatography," Academic Press, New York and London (1963), a) p. 200; b) p. 56.

16) Z. Dische, *Mikrochemie*, **8**, 4 (1930).

17) M. Renoll and M. S. Newman, "Organic Syntheses," Coll. Vol. III, p. 502 (1955).

18) A. Wohl and C. Neuberg, *Ber.*, **33**, 3095 (1900).

19) Footnote 14 in H. O. Fischer, C. Taube, and E. Baer, *Ber.*, **60**, 482 (1927).

20) W. F. Gresham and W. E. Grigsby, *J. Org. Chem.*, **14**, 1103 (1949).

21) H. Reich and B. K. Samuels, *ibid.*, **21**, 68 (1956).

22) H. B. Henbest, E. R. H. Jones, and I. M. S. Walls, *J. Chem. Soc.*, **1950**, 3646.

was washed with a saturated sodium chloride solution and dried (sodium sulfate). The residue obtained by evaporation of the solvent under reduced pressure was subjected to a vacuum distillation to give pure V as colorless liquid, bp 123—128°C/2 mmHg, n_D^{20} 1.4864, 57.9 g (73.5%) [lit,[23] bp 125—126°C/0.7 mmHg, n_D^{21} 1.4873]. IR (neat): 3440 (O–H), 2230 (–C≡C–), 902, 870, 815 (tetrahydropyranyl) cm^{-1}.

Found: C, 65.00; H, 8.72%. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75%.

5-(Tetrahydro-2-pyranyloxy)-3-cis-*penten-1-ol (VI).* The acetylenic alcohol (V, 27.6 g, 0.15 mol) in ethyl acetate (150 m*l*) was reduced over Lindlar catalyst[9] (5.75 g) under an atomspheric pressure of hydrogen at room temperature. The uptake of hydrogen ceased after 4.5 hr (3520 m*l*, Calcd 3480 m*l*). The liquid obtained by evaporation of the solvent under diminished pressure was distilled *in vacuo* to yield pure VI as colorless liquid, bp 120—125°C/3 mmHg, n_D^{20} 1.4774, 25.0 g (90%), IR (neat): 3420 (O–H), 3015 (=C–H), 1662 (–C=C–), 902, 868, 814 (tetrahydropyranyl) cm^{-1}.

Found: C, 64.47; H, 9.71%. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74%.

2-Deoxy-5-O-(tetrahydro-2-pyranyl)-DL-erythro-*pentitol (VII).* To a solution of the ethylenic alcohol (VI, 45 g, 0.24 mol) in ethanol (450 m*l*) maintained at −40°C was added under vigorous agitation a solution of potassium permanganate (37.9 g, 0.24 mol) in water (700 m*l*) over a period of 13.5 hr. During this period, the temperature of reaction mixture was raised gradually to −20°C. After standing overnight, the reaction mixture was stirred at 35°C for 1 hr. Manganese dioxide was collected by filtration and washed with hot water. The combined filtrate and washings were salted out by the addition of anhydrous potassium carbonate. The organic layer was separated, and the aqueous layer was extracted with ether. The aqueous layer was then extracted with the same solvent for 24 hr using a continuous extractor. The organic layer was combined with the extracts and washed with a saturated solution of sodium chloride and dried (sodium sulfate). Evaporation of the solvent under reduced pressure afforded a light brown viscous syrup, 27.4 g (61%), tlc (solvent: ethyl acetate; detection reagent: A): R_f 0.15 (strong), 0.27 (weak), 0.35 (weak), 0.55 (medium), IR (neat): 3370 (O–H), 910, 870, 810 (tetrahydropyranyl) cm^{-1}. The spots at R_f 0.15 and 0.55 seem to be attributable to VII and VI, respectively. Since the purification was found to be difficult, the crude VII thus prepared was subjected to the following reaction.

2-Deoxy-3,4-O-isopropylidene-5-O-(tetrahydro-2-pyranyl)-DL-erythro-*pentitol (VIII).* A mixture of the crude VII (3.518 g), anhydrous cupric sulfate (17.6 g) and anhydrous acetone (352 m*l*) was stirred at room temperature. At 2 hr intervals, small samples of the solution were took out and examined by tlc (solvent: ethyl acetate; detection reagent: A). As soon as the spot of VII had disappeared (usually after 4—8 hr), cupric sulfate was removed by filtration to halt the reaction. The filtrate was concentrated under reduced pressure to give a pale yellow liquid (3.394 g). Tlc of the liquid exhibits a main spot at R_f *ca.* 0.7 and a minor spot at R_f *ca.* 0.9 (solvent: ethyl acetate; detection reagent: A). A 1 g-portion of the pale yellow liquid was chromatographed on alumina (E. Merck, activity III—IV, 100 g). The column was eluted with ethyl acetate and the eluant was fractionally collected (each 7 m*l*). The fractions 8 and 9 were homogeneous on tlc (R_f 0.9). The fraction 11 gave one spot at R_f 0.7, whereas the fractions 12—17 were found to be a mixture of two components (R_f 0.7 and 0.65). On evaporating the solvent under reduced pressure, the fraction 11 gave fairly pure VIII as a syrup (96 mg), IR (neat): 3420 (O–H), 1389, 1378, 845 (dimethyldioxolane), 907, 870, 810 (tetrahydropyranyl) cm^{-1}. NMR (DMSO-d_6): δ 1.26 (3H, s) CH_3, δ 1.31 (3H, s) CH_3, 4.55 (1H, broad s) $-CH\langle^{O}_{O}$.

Found: C, 60.99; H, 9.27%. Calcd for $C_{13}H_{24}O_5$: C, 59.98; H, 9.29%.

2-Deoxy-N-phenyl-DL-erythro-*pentosylamine.* *a) By the Barton's Oxidation*: Syrupy crude VIII (286 mg) obtained from the fractions 11—17 and quinoline (171 mg) were dissolved in anhydrous ether (20 m*l*). The solution was chilled on an ice-salt bath, into which a rapid stream of purified phosgene was introduced for 10 min. The reaction mixture was then stirred for 1 hr at 20°C. Quinoline hydrochloride deposited was filtered with the aid of slightly elevated air pressure avoiding atmospheric humidity. Concentration of the filtrate under reduced pressure yielded chloroformate as light yellow liquid [IR (neat): 1780 (Cl–C=O) cm^{-1}]. The crude chloroformate (355 mg) was mixed with dimethyl sulfoxide (5 m*l*) under stirring and external cooling (bath temperature: 10—15°C). After the exothermic reaction with evolution of carbon dioxide had subsided, the cooling bath was removed and the mixture was stirred at 20°C for 15 min. Then the ice-cooled reaction mixture was mixed with triethylamine (0.185 m*l*) and kept for 3 min at the same temperature. After stirring for 20 min at 20°C, amine hydrochloride deposit was removed. The filtrate was mixed with water (15 m*l*) under cooling, and extracted repeatedly with ether and dried (sodium sulfate). Evaporation of the solvent under diminished pressure gave a pale yellow liquid (205 mg). A mixture of the liquid (203 mg) and 0.1N hydrochloric acid (5 m*l*) was stirred overnight at room temperature. The liquid gradually dissolved in aqueous layer. After 18 hr, the mixture was treated with Dowex-3 (OH^-) to remove chloride ion, and 2-hydroxytetrahydropyran formed was extracted with ether. The aqueous layer was concentrated under reduced pressure at a temperature below 35°C. The syrupy residue was dried *in vacuo* over phosphorus pentoxide, yielding crude 2-deoxy-DL-*erythro*-pentose (IX, 89 mg). Tlc (solvent: acetone; detection reagent: B or C) gave a spot at R_f 0.60 which corresponds with that of an authentic D-isomer. A mixture of the syrupy IX (76 mg), aniline (0.103 m*l*), methanol (0.2 m*l*) and water (0.2 m*l*) was seeded with a trace amount of crystals of the anilide obtained from an authentic DL-IX and the mixture was kept in a refrigerator for a week. The crystals deposited were collected by filtration and washed with 50% aqueous methanol and ether, and then dried to yield the anilide of DL-IX as colorless leaflets (1 mg), mp 157—162°C (decomp.). The anilide thus obtained gave identical IR spectrum with that of the anilide by the method (b). (see, below).

b) By Hydroboration of DL-erythro-*4-Pentyn-1,2,3-triol (XI)*: A solution of bis(1,2-dimethylpropyl)borane was prepared according to the usual manner from a solution of 2-methyl-2-butene (4.6 g, 62.4 mmol) in tetrahydrofuran (20 m*l*) and a diborane stock solution (26.9 m*l*, 15.6 mmol). To the stirred solution of bis(1,2-dimethylpropyl)borane which was strongly cooled on an ice-salt bath was added in an atmosphere of nitrogen a solution of pentyn-triol (XI, 697 mg, 6 mmol) in tetrahydrofuran (5 m*l*) accompanying with evolution of hydrogen. The mixture was stirred for 30 min under ice-cooling, then for 2 hr at room temperature. After standing overnight at room temperature, water (120 m*l*) was added under ice-cooling and stirring. Hydrogen peroxide (15%, 13.6 m*l*) was then added dropwise over a period of 20 min to the

23) L. P. Wells, Istraeli 9220, *Chem. Abstr.*, **52**, 20058 (1958).

vigorously stirred mixture, simultaneously 1N sodium hydroxide solution was added in amall drops to keep the pH of mixture at 7.0—7.5. Further stirring was continued for 30 min under ice-cooling, then for 4 hr at room temperature. In order to decompose the excess of hydrogen peroxide, 1N sodium hydrogen sulfite solution was added to the ice-cooled mixture in 1 m*l* portion until the mixture gave negative iodine-starch test. The resulting solution was treated with Amberlite IR 200 (H^+) and Dowex-3 (OH^-) to remove sodium and sulfate ions. The deionized solution was evaporated *in vacuo* at a temperature below 35°C. The residue, a mixture of syrupy liquid and crystalline boric acid, was mixed with methanol, and evaporated under reduced pressure. The procedure was repeated 3 times to remove boric acid as methyl ester. The residue was dried *in vacuo* over phosphorus pentoxide to yield crude 2-deoxy-DL-*erythro*-pentose (IX) as a syrup (750 mg). The syrupy IX (369 mg) was mixed with aniline (0.256 m*l*), ethanol (2.13 m*l*) and waer (0.99 m*l*) and kept in a refrigerator. After 2 days, 90 mg of crystals of the anilide deposited, and second crop of the anilide (36 mg) was obtained from the mother liquor. [Total yield: 20% based on the acetylenic triol (XI)]. The crystals were recrystallized from methanol to afford colorless plates, mp 157—160°C (decomp.). [lit,[8] mp 154—155°C]. The IR spectrum of the anilide was found to be identical with those of anilides derived from an authentic D-IX and DL-IX prepared by a different route.[13] IR (Nujol mull): 3330, 3260 (OH, NH), 1606, 1500, 1445, 760, 698 (aromatic) cm^{-1} (*Cf.*, Fig. 1).

2-Deoxy-erythro-*pentose (IX).* According to the usual method,[24] a mixture of anilide (75 mg), benzaldehyde (0.075 m*l*), benzoic acid (7.5 mg) and water (2.25 m*l*) was stirred at room temperature for 22 hr, and then extracted 3 times with ether. The aqueous layer was concentrated *in vacuo* at a temperature below 35°C, thus yielding a colorless syrup. After the syrup had been kept over phosphorus pentoxide *in vacuo*, a small amount of ethyl acetate was added. The mixture crystallized on seeding with a trace of crystals of an authentic D-IX. The crystalline DL-IX (44 mg, 92%) was recrystallized from ethyl acetate to yield pure DL-IX, mp 86—89°C, tlc (detection reagent: C): R_f 0.60 (solvent: acetone); R_f 0.74 (solvent: methanol). The R_f values were found to be identical with those of authentic DL-IX and D-IX prepared by a different method.[13]

Found: C, 45.03; H, 7.52%. Calcd for $C_5H_{10}O_4$: C, 44.77; H, 7.52%.

The authors gratefully acknowledge to Mr. Tokusuke Egawa, the president of Kofuku-sogo Bank, for financial support.

24) E. Hardegger, "Methods in Carbohydrate Chemistry," Vol. 1, ed. by R. L. Whistler and M. L. Wolfrom, Academic Press, New York and London (1962), p. 178.