288. *Deoxy-sugars. Part IV. A Synthesis of 2-Deoxy-D-ribose from D-Erythrose.*

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The synthesis of 2-deoxy-D-ribose from D-erythrose as the initial material is described. Several methods of obtaining D-erythrose are outlined, and a method for its purification is discussed.

The difficulty in preparing 2-deoxy-D-ribose, the deoxypentose of deoxyribonucleic acid, and hence a sugar of great biological importance, has hitherto prevented a systematic study of its derivatives. We have now studied many possible methods of its synthesis. Two of the methods investigated have already been reported. One concerned a study of the catalytic reduction of 2-bromo β-methylarabinoside, which was obtained, together with 3-bromo β-methylxyloside, by treating 2 : 3-anhydro-β-methyl-D-riboside with hydrogen bromide, and the other involved the methanesulphonyl derivatives of D-arabopyranoside (Parts II and III).

Recently, Fischer and Sowden (*J. Amer. Chem. Soc.*, 1947, **69**, 1048) showed that when D-arabinose is treated with nitromethane and an acetylating agent it yields 1-nitro-D-*arabo*-3 : 4 : 5 : 6-tetra-acetoxyhex-1-ene, reduction of which gave 1-nitro 1 : 2-dideoxy-D-arabohexityl tetra-acetate (1-nitro-3 : 4 : 5 : 6-tetra-acetoxyhexane). Treatment of this compound with sodium hydroxide and then dilute sulphuric acid resulted in simultaneous elimination of the nitro-group and deacetylation and afforded 2-deoxy-D-glucose. It was apparent that if D-erythrose were used in the synthesis instead of D-arabinose, then a route to the synthesis of 2-deoxy-D-ribose would be provided. Consequently, various methods of making D-erythrose from easily accessible carbohydrates have been investigated.

Several methods have been described for the preparation of L-erythrose. Deulofeu and Selva (*J.*, 1929, 225) summarised methods which have been used to degrade L-arabinose to L-erythrose and outlined their own extensions of these methods, these being directed mainly towards

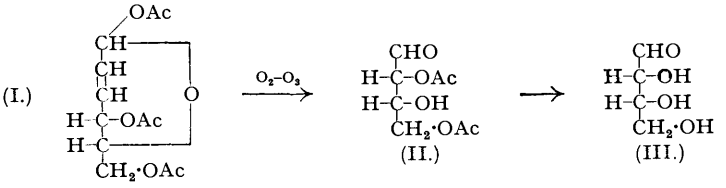
degrading L-arabonic acid by Ruff's method. More recently, Felton and Freudenberg (*J. Amer. Chem. Soc.*, 1935, **57**, 1637) treated L-arabinal with ozonised oxygen and obtained L-erythrose, and DL-erythrose has been prepared by the reduction of DL-erythronolactone by Glattfeld and Kribben (*ibid.*, 1939, **61**, 1720). There is very little information in the literature about methods of preparing the D-isomer.

When starch is oxidised by periodic acid it gives a polymeric dialdehyde (Jackson and Hudson, *ibid.*, 1937, **59**, 2049) which when hydrolysed with hydrochloric acid yields glyoxal and D-erythrose. [When methanolic hydrogen chloride is used for the hydrolysis, then one of the isomeric hexahydro-3 : 5-dimethoxy-2-(1-methyl-2- or 3-erythrofuranosyloxy)-furo-(3 : 4)-*p*-dioxins is also obtained (Michell and Purves, *ibid.*, 1942, **64**, 585).] Jackson and Hudson (*ibid.*, 1938, **60**, 989) did not isolate free D-erythrose, but oxidised the hydrolysis mixture with bromine-water, thereby obtaining oxalic acid (from the oxidation of glyoxal) and D-erythronic acid, isolated as its brucine salt. This was converted into D-erythronolactone obtained in an overall yield from starch of 7% of the theoretical. We have repeated this method in an attempt to obtain, in improved yield, a suitable derivative of D-erythrose from starch.

Potato starch was oxidised at 20—25° with an aqueous solution of periodic acid. The course of the oxidation was followed titrimetrically and was complete in 6 days. The oxidised starch was a coarse white powder, strongly reducing to Fehling's solution in the cold. It was hydrolysed with N-hydrochloric acid at 98—99° for 16 hours, and the hydrolysate then oxidised with bromine-water, thereby forming D-erythronic acid, isolated as the brucine salt in a yield of 33% of the theoretical: Hudson and Jackson (*loc. cit.*) obtained a 22% yield. It was found that D-erythronolactone could readily be purified through its 2 : 3-diacetyl derivative, although the overall yield of 2 : 3-diacetyl D-erythronolactone from starch was not much greater than that obtained by Hudson and Jackson (*loc. cit.*). Since this yield was so unsatisfactory attempts were made to utilise compounds derived from D-glucose.

Calcium D-gluconate was degraded to D-arabinose essentially by Hockett and Hudson's method (*ibid.*, 1934, **56**, 1632). Oxidation of this pentose with bromine-water gave D-arabonic acid (isolated as its calcium salt) in good yield. Hockett and Hudson's method of degradation (*loc. cit.*) was applied to calcium D-arabonate and it yielded D-erythrose as a pale yellow immobile syrup, which strongly reduced Fehling's solution. It could not be induced to crystallise or to form a solid phenylosazone. Purification was effected by converting it into 2 : 3-*iso*propylidene αβ-methyl-D-erythroside ($[\alpha]_D^{14\cdot5°}$ −55·5° in chloroform) by treatment with dry acetone and methyl alcohol containing 0·2% sulphuric acid and anhydrous copper sulphate. This erythroside was a pale yellow liquid which was purified by distillation in a vacuum as described by Felton and Freudenberg (*loc. cit.*) for purifying the L-isomer. Its hydrolysis with 0·1N-sulphuric acid at room temperature resulted in scission of the *iso*propylidene group and elimination of the glycoside residue, giving D-erythrose as a pale yellow syrup which was completely soluble in ethyl alcohol and which now formed a solid phenylosazone. D-Erythrose shows mutarotation in aqueous solution, equilibrium at −19·1° being reached after 73 hours (initial value −1·2°). At various times different values (see p. 1361) have been reported for the rotation of erythrose, and it seems that the true rotation of D-erythrose cannot be determined until the compound has been obtained in the crystalline state.

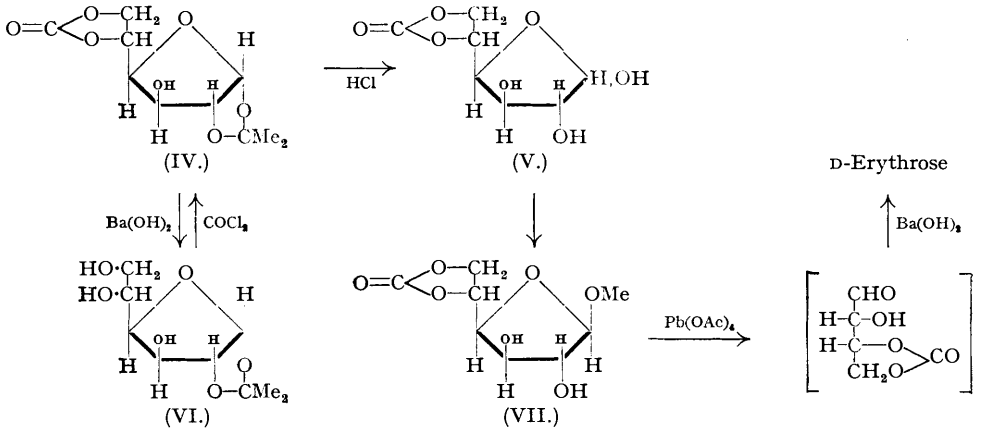
Two other methods of preparing D-erythrose from compounds derived from D-glucose were also carried out. It was shown by Bergmann, Kobel, Schotte, Rennert, and Ludewig (*Annalen*, 1923, **434**, 79) that when triacetyl glucal is boiled with water, the ethylenic linkage between C_1 and C_2 migrates to the position between C_2 and C_3 and acetylation of the product (later shown



to be diacetyl *pseudo*glucal; Bergmann, *ibid.*, 1925, **443**, 223) with acetic anhydride and sodium acetate gives triacetyl *pseudo*glucal (I). This was prepared (for physical constants, see p. 1362) and submitted to ozonisation. Scission of the ethylenic linkage occurred and there was obtained syrupy 2 : 4-*diacetyl* aldehydo-D-*erythrose* (II), hydrolysis of which with hydrochloric acid gave D-erythrose ($[\alpha]_D^{1\cdot75°}$ −19·7°, equilibrium) which was sufficiently pure readily to form a

solid phenylosazone. It was shown incidentally that catalytic hydrogenation of triacetyl *pseudo*glucal gives 1 : 4 : 6-*triacetyl* 2 : 3-*dideoxyglucopyranose*.

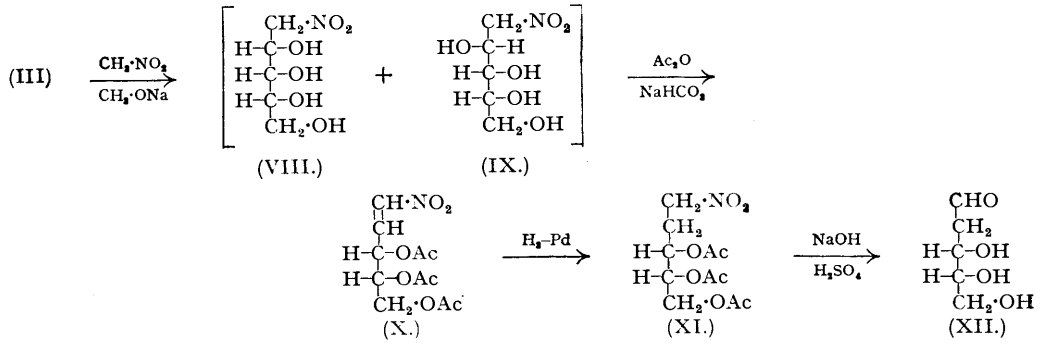
In another route to erythrose, treatment of glucose in suspension in dry acetone with carbonyl chloride gave 1 : 2-*iso*propylidene glucofuranose 5 : 6-carbonate (IV) (Haworth and Porter, *J.*, 1929, 2801). Since it can be prepared similarly from 1 : 2-*iso*propylidene



glucofuranose (VI), its structure follows. The action of hydrochloric acid on (IV) resulted in scission of the *iso*propylidene group and gave glucofuranose 5 : 6-carbonate (V). Treatment of this with methyl alcohol containing sulphuric acid afforded β-methylglucofuranoside 5 : 6-carbonate (VII) (cf. Haworth and Porter, *loc. cit.*). This was oxidised with excess of lead tetra-acetate, and the syrupy reaction product was heated with barium hydroxide solution, yielding D-erythrose ($[\alpha]_D^{18°}$ −17·6°, equilibrium), but only in low yield. Of the four methods outlined for the preparation of D-erythrose, the best yield was afforded by the degradation of calcium D-arabonate by Ruff's procedure.

It was of interest to find that (IV) formed crystalline 3-*methanesulphonyl* 1 : 2-iso*propylidene glucofuranose* 5 : 6-*carbonate* (m. p. 136—137°) when treated with methanesulphonyl chloride in dry pyridine, though as expected, treatment of this with dry acetone and sodium iodide in a sealed tube at 110° for 5 hours failed to give direct replacement of the methanesulphonyl group by an iodine atom.

D-Erythrose (III) was treated with nitromethane and sodium methoxide, giving a mixture of D-*ribo*- and D-*arabo*-1-nitropentitol (VIII and IX, respectively). These were not separated,



but the mixture was heated under reflux with acetic anhydride and sodium hydrogen carbonate and yielded 1-*nitro*-D-erythro-3 : 4 : 5-*triacetoxypent*-1-*ene* (X), isolated in crystalline state. This was reduced in methanolic solution at room temperature with hydrogen in the presence of a palladium-black catalyst, and then treated with sodium hydroxide followed by dilute sulphuric acid. The resulting syrup was heated with aniline in ethyl alcohol and water, and on standing 2-deoxy-D-ribose anilide was deposited. De-anilination was effected by treating the anilide with 0·5% oxalic acid solution in water, and there was obtained 2-deoxy-D-ribose (XII); anilination of a sample of this re-afforded the anilide.

Experimental.

Oxidation of Starch with Periodic Acid.—A solution of periodic acid in water (0·066 g. per c.c. of solution) was prepared by treating a solution of potassium metaperiodate (75·0 g.) in water (2·5 l.) with a solution of barium acetate monohydrate (89·12 g.) in water (500 ml.) at 70°. The mixture was kept at 5° for 6 hours, and was stirred continuously. Barium metaperiodate separated as a white powder, and was collected by filtration, washed with water until free from acetic acid, and then dried, first in air for 2 days and then at 110°. This product (50 g.) was suspended in water (90 c.c.) and 1·06N-sulphuric acid was added. Removal of the barium sulphate formed yielded an aqueous solution of periodic acid.

Freshly dried starch (13·5 g.) was added to the above periodic acid solution (282 c.c. = 18·8 g. HIO_4) and the mixture was shaken at 20—25°. The course of the oxidation was followed volumetrically and was complete in 144 hours. The polymeric dialdehyde was collected by filtration and washed with cold water to remove excess of periodic and iodic acids. The oxidation product was dried at 35° and was a white powder, coarse to the touch and strongly reducing in the cold to Fehling's solution; $[\alpha]_D^{24°}$ +9·5° (*c*, 0·209 in water): Hudson and Jackson (*J. Amer. Chem. Soc.*, 1937, **59**, 2049) give $[\alpha]_D^{20}$ +9°.

Hydrolysis of Oxidation Product.—The above product (12·5 g.) was heated with water (500 c.c.) at 100° for 3 hours, and the solution filtered. N-Hydrochloric acid (75 c.c.) was added to the filtrate which was diluted to 750 c.c. and kept at 98—99° for 16 hours, in a stoppered flask. The course of the hydrolysis was followed polarimetrically, but this procedure became increasingly difficult towards the end of the reaction as the solution became strongly coloured. After treatment with charcoal, bromine (20 ml.) was added, and the solution was kept for 4 days at room temperature in the dark. Excess of bromine was removed by aeration and the solution was neutralised with barium hydroxide. The barium oxalate formed was removed by filtration and excess of barium ions in the filtrate was removed by addition of 1N-sulphuric acid. Chloride ions present were removed with silver carbonate, and then silver ions in solution were precipitated by passage of hydrogen sulphide, excess of which was removed by boiling. When all extraneous ions had been removed from the solution, it was concentrated under diminished pressure to 200 c.c., and ethyl alcohol (50 c.c.) was added together with excess of brucine (50 g.). The solution was heated on a steam-bath for 3 hours and then the excess of brucine was extracted with chloroform. The aqueous residue was evaporated to a thick syrup, which on trituration with ethyl alcohol yielded amorphous brucine erythronate (15·2 g., 33%) which could not be induced to crystallise.

2 : 3-*Diacetyl* D-*Erythronolactone*.—Crude brucine D-erythronate (3·0 g.) was treated with excess of oxalic acid, the liberated brucine was extracted with chloroform, and excess of oxalate ions removed by adding calcium hydroxide. The filtered solution was evaporated to dryness under diminished pressure. The residue was added at 0° to freshly distilled acetic anhydride (25 c.c.) containing dry hydrogen chloride (0·6 g.), and the mixture shaken. The temperature was gradually allowed to increase to room temperature and kept thereat for 3 hours. Excess of acetic anhydride was removed by distillation under diminished pressure, and the residue was distilled as a colourless syrup, b. p. 200° (bath temp.)/12 mm., which slowly crystallised. After recrystallisation from hot water, it had m. p. 50—51·5°; yield 0·22 g. (22%). Glattfeld and Kribben (*loc. cit.*) give m. p. 53° for diacetyl DL-erythronolactone.

Calcium D-*Arabonate*.—D-Arabinose (117·40 g.) was dissolved in water (588 c.c.), and bromine (78·4 c.c.) added. The solution was kept for 2 hours, and then the excess of bromine was removed by aeration. The hydrogen bromide formed during the reaction was removed by adding silver oxide, and filtering off the precipitated silver bromide. Any silver in solution was precipitated with hydrogen sulphide, and the solution was boiled with calcium carbonate for 15 minutes. The filtered solution was evaporated to give a crystalline residue, which recrystallised from water in white needles (123·4 g.; 85·2%); m. p. 99—101°, $[\alpha]_D^{21°}$ −6·8° (*c*, 2·645 in water).

D-*Erythrose*.—Barium acetate monohydrate (14·89 g.), dissolved in water (43 c.c.), and ferric sulphate (7·31 g.), also dissolved in water (43 c.c.), were slowly added to water (1·42 l.) in equimolecular portions with stirring. The resulting solution was slowly boiled and calcium D-arabonate (123·40 g.) was slowly added to it. When the addition was complete the solution was boiled for 20 minutes and then filtered through a carbon pad and cooled to 40°; hydrogen peroxide (86·04 c.c., 100-vol.) was then added. The temperature rose to 60° and the solution became dark. After it had been again cooled to 40°, a second portion of hydrogen peroxide was added (86·04 c.c.) and the mixture was set aside overnight. Then it was filtered through a charcoal pad, and the filtrate was concentrated under diminished pressure to 160 c.c. Methyl alcohol (1075 c.c.) was added to it, and the solid which separated was removed by filtration. The residue was washed with methyl alcohol (215 c.c.) and the washings were added to the filtrate. Ether (645 c.c.) was added to the methyl-alcoholic extract, and after standing for 5 minutes, it was refiltered. Removal of the solvent from the filtrate by evaporation yielded a pale yellow syrup which set to a glass. The syrup was strongly reducing to Fehling's solution. Trituration with either methyl alcohol or glacial acetic acid did not induce crystallisation. The changes of rotation (*c*, 3·244 in water) were as follows:

Time, hours	—	0·166	0·65	2·50	3·63	23·38	49·23	73·23	97·23
$[\alpha]_D^{14·5°}$	−1·23°	−2·46°	−4·31°	−5·24°	−11·09°	−11·71°	−14·79°	−18·5°	−18·5°

Felton and Freudenberg (*loc. cit.*) give +30·5° after 2 days for the L-isomer; Wohl (*Ber.*, 1899, **32**, 3667) gives +32·7°; Weerman (*Rec. Trav. chim.*, 1917, **37**, 15) +23·6°; Deulofeu (*J.*, 1932, 1973) +22·1°; Ruff (*Ber.*, 1901, **34**, 1365) +21·5°. Further, for $[\alpha]_D$ for D-erythrose, Ruff (*Ber.*, 1899, **32**, 3672) gives −14·8° and Weerman (*Rec. Trav. chim.*, 1932, **37**, 16) −14·5°.

The syrup (yield 35 g., 46%) (Found: C, 39·6; H, 6·8. Calc. for $C_4H_8O_4$: C, 40·0; H, 6·66%) was shown to be D-erythrose by conversion into *iso*propylidene methylerythroside and into erythrosazone.

2 : 3-iso*Propylidene αβ-Methyl-*D-*erythroside*.—D-Erythrose syrup (4·51 g.), dry acetone (100 ml.), dry methyl alcohol (10 ml.) containing 0·2% sulphuric acid, and anhydrous copper sulphate (10 g.) were shaken together overnight. After filtration, the filtrate was neutralised with barium carbonate and then refiltered. Removal of the solvents by evaporation gave an oily residue, which distilled as a pale yellow liquid, b. p. 100° (bath temp.)/10 mm.; $[\alpha]_D^{14·5°}$ −55·5° (*c*, 0·054 in chloroform) (Found: OMe, 17·3.

Calc. for $C_8H_{14}O_4$: OMe, 17·8%) (2 : 3-*iso*propylidene methyl-L-erythroside has b. p. 45—50°/2 mm., $[\alpha]_D$ +57·4° in chloroform; Felton and Freudenberg, *loc. cit.*). This liquid (4·0 g., 61%) was non-reducing to Fehling's solution in the cold, but on heating for a few minutes it suddenly reduced the solution.

Hydrolysis of 2 : 3-iso*Propylidene αβ-Methyl*-D-*erythroside.*—This erythroside (1 g.) was dissolved in 0·1N-sulphuric acid, and the solution kept at room temperature for 3 days, the rotation then being constant. Glacial acetic acid (1·5 c.c.) was added, and the sulphate ions were removed by adding barium hydroxide solution. The solution, filtered through charcoal, was evaporated to dryness. There remained a pale yellow viscid syrup (0·58 g.) which was completely soluble in ethyl alcohol and strongly reduced Fehling's solution in the cold; $[\alpha]_D^{17°}$ −19·1° (equilibrium in 3 days) (*c*, 2·14 in water); cf. $[\alpha]_D^{14·5°}$ −18·5° for D-erythrose.

D-*Erythrose Phenylosazone.*—The foregoing syrup (0·5 g.) was dissolved in ethyl alcohol (5 c.c.) and to it was added a solution of phenylhydrazine (1·4 g.) in glacial acetic acid. The mixture was heated on a water-bath for 30 minutes and then poured into water. An oil separated, which was washed with water by decantation. After two days, the oil solidified, and was collected and recrystallised from ethyl alcohol, forming a yellow powder (0·35 g.), m. p. 160—162·5°; Felton and Freudenberg (*loc. cit.*) give m. p. 160—163°.

1 : 4 : 6-*Triacetyl* pseudo*Glucal.*—Triacetyl glucal (12·95 g.) was heated under reflux for 15 minutes with water (259 g.), and the solution concentrated under diminished pressure. The syrupy residue was taken up in ether, and the solution washed with sodium hydrogen carbonate solution and dried ($MgSO_4$). After distillation of the solvent, there were added to the syrupy residue (2·64 g.) freshly distilled acetic anhydride (60 c.c.) and fused sodium acetate (6 g.), and the mixture heated on a boiling water-bath for 3 hours, and then evaporated to dryness under diminished pressure. Ethyl alcohol was distilled twice over the residue, which was afterwards extracted with ether. The ethereal extract was dried ($MgSO_4$), and the solvents removed by distillation. The residue distilled as a pale yellow syrup (1·31 g.); b. p. 115—125°/0·01 mm., $[\alpha]_D^{18·5°}$ +66·8° (*c*, 0·898 in chloroform), $n_D^{19°}$ 1·4839 (Found: C, 52·7; H, 5·9. Calc. for $C_{12}H_{16}O_7$: C, 52·92; H, 5·91%); it decolorised bromine water. Bergmann *et al.* (*Annalen*, 1923, **434**, 79) give b. p. 150—165°/0·2—0·3 mm.

1 : 4 : 6-*Triacetyl* 2 : 3-*Dideoxyglucose* (with Dr. J. Staněk).—1 : 4 : 6-Triacetyl *pseudo*glucal (0·5 g.) was dissolved in absolute ether (50 c.c.) and after addition of palladium catalyst (on charcoal) the solution was hydrogenated under a slight pressure at room temperature. The catalyst was removed by filtration, and then the solvent by evaporation. The residual *triacetyl dideoxyglucose* was a colourless oil, which distilled as a colourless liquid, b. p. *ca.* 120—130°/0·01 mm. (bath temp.), $[\alpha]_D^{15°}$ +32·63° (*c*, 0·8587 in chloroform), $n_D^{15°}$ 1·4548 (Found: C, 52·6; H, 6·9. $C_{12}H_{18}O_7$ requires C, 52·55; H, 6·6%).

Ozonisation of 1 : 4 : 6-*Triacetyl* pseudo*Glucal.*—Triacetyl *pseudo*glucal (0·595 g.) was dissolved in glacial acetic acid (10 ml.) and a stream of oxygen–ozone was passed through the solution at 12°, until it no longer decolorised a solution of bromine in carbon tetrachloride. After dilution with ether (30 c.c.), zinc dust (10 g.) was added, and the mixture heated under reflux until the solution failed to colour starch–iodide paper. After filtration, the ether was removed by evaporation, and the acetic acid by distillation with alcohol. The residue, which was strongly reducing to Fehling's solution, was extracted with alcohol containing a few drops of water. Removal of the solvent from the extract gave 2 : 4-*diacetyl* D-*erythrose* as a colourless syrup (0·42 g., 95·4%). Trituration with ethyl alcohol and refrigeration did not induce crystallisation; $n_D^{16°}$ 1·4711, $[\alpha]_D^{17·5°}$ −20·9° (*c*, 0·572 in chloroform) (Found: C, 46·5; H, 5·5. $C_8H_{12}O_6$ requires C, 47·0; H, 5·8%).

Hydrolysis of 2 : 4-*Diacetyl* aldehydo-D-*Erythrose.*—The diacetyl compound (0·2 g.) and 0·05 N-hydrochloric acid were heated together under reflux for 5 hours. The solution was neutralised with barium carbonate, the filtered solution evaporated to dryness, and the residue extracted with ethyl alcohol. The extract was again evaporated to dryness, and the procedure repeated twice more. A pale yellow syrup (0·08 g.) remained which was strongly reducing to Fehling's solution; $[\alpha]_D^{17·5°}$ −19·7° (*c*, 2·47 in water; equilibrium value); phenylosazone, m. p. 160—163° alone or in admixture with D-erythrose phenylosazone.

1 : 2-iso*Propylidene Glucofuranose* 5 : 6-*Carbonate.*—Anhydrous glucose (16 g.) was suspended in freshly dried acetone (150 c.c.), and carbonyl chloride was passed through the suspension for 10 hours. After standing overnight, unchanged glucose (6·4 g.) was removed by filtration. The filtrate was neutralised with basic lead carbonate and then refiltered. The residue was washed with acetone, and the washings added to the filtrate. The volume of the solution was reduced to 10 c.c. and the solid which separated was collected and recrystallised from absolute ethyl alcohol, forming colourless needles (4·70 g.), m. p. 226° (sinters 215—216°), $[\alpha]_D^{20°}$ −37·4° (*c*, 0·560 in ethyl alcohol). Haworth and Porter (*loc. cit.*) give m. p. 223—224° (decomp.), $[\alpha]_{5780}^{20°}$ −36°.

3-*Methanesulphonyl* 1 : 2-iso*Propylidene Glucofuranose* 5 : 6-*Carbonate.*—The dry carbonate (above) (0·7812 g.) was dissolved in dry pyridine (10 c.c.), the solution cooled to 0°, and methanesulphonyl chloride (1·1 mols., 0·401 g.) slowly added. The mixture was left at room temperature overnight, and then poured into water and extracted with chloroform. The extract was dried ($CaCl_2$) and then evaporated to dryness. A syrup remained which crystallised on trituration with ethyl alcohol. Recrystallisation from ethyl alcohol yielded long colourless needles of the *methanesulphonyl* derivative (0·95 g., 92·2%); m. p. 136—137°, $[\alpha]_D^{18·5°}$ −22·1° (*c*, 0·452 in chloroform) (Found: C, 40·7; H, 5·0; S, 9·7. $C_{11}H_{16}O_9S$ requires C, 40·7; H, 4·9; S, 9·9%).

Glucofuranose 5 : 6-*Carbonate.*—1 : 2-*iso*Propylidene glucofuranose 5 : 6-carbonate (0·6 g.) was dissolved in ethyl alcohol (17 c.c.) containing concentrated hydrochloric acid (0·83 c.c.), and the solution heated at 70—75° for 40 minutes. On cooling, crystals separated; these were filtered off and shown to be unchanged material (0·3 g.). The filtrate was evaporated at 45—50° and water (30 c.c.) was gradually added so that the total volume did not fall below 17 c.c. After this treatment the solution was neutralised with silver carbonate and filtered. The filtrate was concentrated to dryness, and the residue extracted with hot methyl alcohol. The solvent was removed by evaporation, and the residue recrystallised from methyl alcohol in small crystals; m. p. 179°, $[\alpha]_D^{17°}$ +18·1° (*c*, 0·442 in water); yield 0·2 g., 68·3% based on the material undergoing change (Found: C, 40·9; H, 5·4. Calc. for $C_7H_{10}O_7$: C, 40·8; H, 4·9%). Haworth and Porter (*loc. cit.*) give m. p. 181°, $[\alpha]_{5780}^{20°}$ +18° in water.

1 : 2-*iso*Propylidene glucofuranose 5 : 6-carbonate (0·5 g.) with excess of barium hydroxide solution at 70° yields 1 : 2-*iso*propylidene glucofuranose, m. p. 158—159°, $[\alpha]_D^{16.5°}$ −13·6° (*c*, 0·292 in water).

β-Methylglucofuranoside 5 : 6-Carbonate.—The foregoing carbonate (1 g.) was dissolved in methyl alcohol (25 c.c.) containing sulphuric acid (0·3 c.c.). After 5 hours at 45° the solution was exactly neutralised with barium carbonate, filtered, and evaporated to dryness under diminished pressure. The residue was dissolved in methyl alcohol, filtered, and ether added. The methylglucofuranoside 5 : 6-carbonate separated, and was filtered off and recrystallised from methyl alcohol–ether; m. p. 142—144°, $[\alpha]_D^{22°}$ −64° (*c*, 0·7 in water); yield 0·8 g. (Found: OMe, 14·7. Calc. for $C_8H_{12}O_7$: OMe, 14·1%). Haworth and Porter (*loc. cit.*) give m. p. 143—145°, $[\alpha]_{5780}^{22°}$ −66°.

Oxidation of β-Methylglucofuranoside 5 : 6-Carbonate with Lead Tetra-acetate.—The carbonate (0·8 g.) was dissolved in dry benzene (10 ml.), and lead tetra-acetate (2 g., 2 mols.) suspended in glacial acetic acid was added. The mixture was kept at 0° for 7 days and then poured into water. The product was extracted with light petroleum (b. p. 60—80°), and the extract washed with water, dried, and evaporated to dryness. A syrup remained, which was heated at 70° for 30 minutes with aqueous barium hydroxide solution. A white precipitate separated, and was removed by filtration. Carbon dioxide was passed through the filtrate, and the barium carbonate precipitated was filtered off. The filtrate was evaporated to dryness and yielded a pale yellow syrup which set to a glass (0·2 g.); $[\alpha]_D^{18°}$ −17·6° (equilibrium in 72 hours) (*c*, 1·45 in water). The syrup yielded a phenylosazone, m. p. 160—162°, identical with D-erythrose phenylosazone.

1-*Nitro*-D-erythro-3 : 4 : 5-*triacetoxypent*-1-*ene.*—D-Erythrose (5·40 g.) was suspended in dry methyl alcohol (50 ml.). To it was added nitromethane (33·7 c.c.), followed by methyl alcohol (50 c.c.) containing sodium (1·42 g.). The mixture was shaken for 24 hours and then diluted with ether (40 c.c.). A solid separated and was filtered off. It was dissolved in water and passed through a Zeocarb-resin column, in order to remove sodium ions. The effluent was evaporated to dryness and yielded a syrupy residue (*A*). To the original filtrate obtained from the above solid, glacial acetic acid (3 c.c.) was added, and the whole evaporated to dryness. The residue was dissolved in water, and the solution passed through a Zeocarb-resin column, to remove sodium ions. The effluent was concentrated to dryness and thoroughly dried in a vacuum desiccator over phosphoric oxide, and the residue was added to (*A*). Redistilled acetic anhydride (excess) and concentrated sulphuric acid (1 drop) were added to this, and the mixture was heated under reflux for one hour. Excess of acetic anhydride was removed by distillation. Dry benzene (150 c.c.) and sodium hydrogen carbonate (15·0 g.) were added to the residue, and the mixture was boiled for 2·5 hours. Filtration and evaporation of the benzene from the filtrate afforded the syrupy *nitropentene* (8·48 g., 65·2%) as a yellow oil; $n_D^{18°}$ 1·4553, $[\alpha]_D^{20°}$ −8·6° (*c*, 1·156 in ethyl alcohol) (Found: C, 45·6; H, 5·15; N, 4·8. $C_{11}H_{15}O_8N$ requires C, 45·6; H, 5·2; N, 4·8%). On attempted distillation, it underwent decomposition at 160—170° (bath temp.)/0·005 mm. After standing for 3 months, the syrup commenced to crystallise. Recrystallisation from alcohol–water gave crystals, m. p. 116—118° (Found: C, 45·2; H, 5·4; N, 4·3%). The material decolorised bromine in alcohol and potassium permanganate solution.

2-*Deoxy*-D-*ribose Anilide.*—The acetylated nitropentene (1·28 g.) was dissolved in dry methyl alcohol (25 c.c.) and palladium-black (0·2 g.) was added. The solution was hydrogenated at room temperature until no further absorption of hydrogen occurred. After filtration, the solution was evaporated to dryness and a thick syrup remained. To this 1N-sodium hydroxide (8 c.c.) was added and the mixture was kept at room temperature for 1 hour. It was then added to a stirred mixture of water (1·5 c.c.) and concentrated sulphuric acid (1·05 c.c.) at room temperature. (At this stage the solution gave a purple Dische reaction.) The solution was neutralised with barium carbonate, stirred with charcoal, filtered, and the filtrate evaporated to dryness. The residue strongly reduced Fehling's solution, and gave a blue Dische colour. It was dissolved in water (2 c.c.) and aniline (0·2 c.c.) was added, together with sufficient ethyl alcohol to make the solution homogeneous. The solution was kept at 0° for 5 days. The ethyl alcohol was removed by evaporation, and on addition of water (5 c.c.) to the residue, a solid separated. This was collected by filtration, and washed with ice-cold ethyl alcohol, but remained faintly yellow; m. p. 175—176°, mixed m. p. with 2-deoxy-D-ribose anilide, 173—174°; $[\alpha]_D$ +20·5° (equilibrium) (*c*, 1·05 in ethyl alcohol); yield 12 mg.

2-*Deoxy*-D-*ribose.*—2-Deoxy-D-ribose anilide (0·125 g.) and 0·5% oxalic acid solution in water (10 c.c.) were heated at 80° for 1 hour. The solution was extracted once with ether to remove aniline, and the aqueous layer was heated under reflux with calcium carbonate. After filtration, the filtrate was evaporated to dryness. The residue was extracted with hot ethyl acetate, and the extract was filtered after standing for some hours. The ethyl acetate was removed by evaporation, and the residue was taken up in dry *iso*propyl alcohol and set aside. Crystals of 2-deoxy-D-ribose separated (0·045 g., 23·3%), m. p. 87—90°, $[\alpha]_D^{22°}$ −55·2° (equilib.) in water (*c*, 0·90). Levene and Mori (*J. Biol. Chem.*, 1929, **83**, 803) give m. p. 80°.

Anilination of 2-*Deoxy*-D-*ribose.*—A suspension of 2-deoxy-D-ribose (0·14 g.) in absolute ethyl alcohol (5 c.c.) was heated under reflux with an alcoholic solution (5 c.c.) of aniline (0·11 g.) for 3 hours, by which time the solid had dissolved. Concentration of the solution by distillation under reduced pressure gave crystals of 2-deoxy-D-ribose anilide (0·19 g., 90%), m. p. 174—175°, $[\alpha]_D^{22°}$ +19·5° (equilibrium) (*c*, 1·05 in ethyl alcohol) (Found: C, 63·25; H, 7·3; N, 6·30. Calc. for $C_{11}H_{15}O_3N$: C, 63·1; H, 7·2; N, 6·7%). Kent, Stacey, and Wiggins (this vol., p. 1232) give m. p. 165—166°.

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