598. *Deoxy-sugars. Part VII. A Study of the Reactions of Some Derivatives of 2-Deoxy-D-Glucose.*

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A re-investigation of methods for the synthesis of 2-deoxy-D-glucose is described, together with the preparation of derivatives. Some of the reactions of these derivatives are outlined and the results of a comparative study of the rates of hydrolysis of the methyl pyrano- and furano-glycosides of 2-deoxyglucose and 2-deoxyribose are discussed.

In continuation of our studies on deoxy-sugars, in particular 2-deoxy-pentoses and -hexoses, we needed 2-deoxy-D-glucose in reasonably large quantities, and consequently we have prepared various crystalline derivatives which serve to characterise further this interesting sugar. Two main methods have been described for the preparation of 2-deoxy-D-glucose. The well-known glycal method was used by Bergmann and Schotte (*Ber.*, 1921, **54**, 440) who treated glucal with dilute acid and isolated 2-deoxyglucose as its phenylbenzylhydrazone. Shortly afterwards these workers obtained the crystalline β-form of the free sugar by cleaving the hydrazone with benzaldehyde (Bergmann, Schotte, and Lechinsky, *Ber.*, 1922, **55**, 158). Recently Sowden and Fischer (*J. Amer. Chem. Soc.*, 1947, **69**, 1048) have developed a method of synthesis which affords mainly the α-form of the sugar. The method involved the treatment of D-arabinose with nitromethane and an acetylating agent which yielded 1-nitro-D-*arabo*-tetra-acetoxyhexene. Reduction of this afforded 1-nitro-1 : 2-dideoxy-D-*arabo*hexitol 3 : 4 : 5 : 6-tetra-acetate, from which 2-deoxy-D-glucose was obtained by treatment with sodium hydroxide. We have made use of both of these methods of synthesis but have concentrated most attention on the former owing to the difficulty of obtaining D-arabinose.

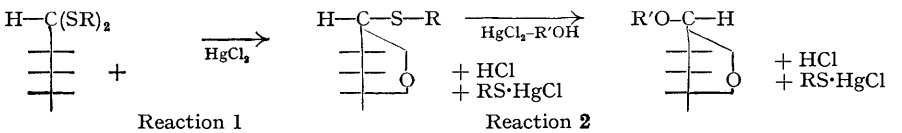
Triacetyl glucal was deacetylated smoothly by dissolving it in methanol containing a trace of sodium, whereby glucal was obtained in excellent yield. This method of deacetylation proved much more convenient than that employed by Bergmann *et al.* (*Ber.*, 1921, **54**, 440) who used methanol saturated at 0° with gaseous ammonia. Treatment of glucal with ice-cold 2N-sulphuric acid gave crystalline 2-deoxy-D-glucose, generally contaminated with syrupy 2-deoxy-D-glucose and other non-crystalline products. The yield of crystalline 2-deoxy-D-glucose was considerably increased by conversion of the syrupy products into the benzyl mercaptal or into the anilide. Crystalline 2-deoxy-D-glucose, toluene-ω-thiol, and concentrated hydrochloric acid gave crystalline 2-*deoxy*-D-*glucose dibenzyl mercaptal*, acetylation of which with acetic anhydride in pyridine

afforded 2-*deoxyglucose dibenzyl mercaptal* 3 : 4 : 5 : 6-*tetra-acetate*. The dibenzyl mercaptal on dissolution in aqueous acetone containing excess of mercuric chloride and yellow mercuric oxide underwent demercaptalation, and crystalline 2-deoxyglucose was regenerated. A suspension of crystalline 2-deoxy-D-glucose in ethanol on reaction with aniline at 80° yielded a crystalline *anilide*, which could be reconverted into the free deoxy-sugar by hot formic acid. These reactions between 2-deoxy-D-glucose and toluene-ω-thiol or aniline take place with syrupy 2-deoxy-D-glucose, for when the whole syrupy material which always accompanies the crystalline deoxyglucose was treated with toluene-ω-thiol it afforded crystalline 2-deoxy-D-glucose dibenzyl mercaptal in 20% yield. Demercaptalation of this by the method already described yielded crystalline 2-deoxy-D-glucose. Similarly, when the syrupy material was treated with aniline in ethanol, it gave crystalline 2-deoxy-D-glucose anilide which afforded 2-deoxy-D-glucose in approximately 20% yield.

A re-investigation of the preparation of 2-deoxy-D-glucose by the method described by Sowden and Fischer (*loc. cit.*) confirmed these authors' claims and resulted in the improvement that we were able to isolate directly the crystalline 2-deoxy-D-glucose without first forming the phenylbenzylhydrazone.

Two further derivatives of 2-deoxy-D-glucose prepared were the α- and β-tetra-acetates. Acetylation of the deoxy-sugar with acetic anhydride in pyridine afforded crystalline 2-*deoxy*-α-D-*glucose* 1 : 3 : 4 : 6-*tetra-acetate* whereas, when sodium acetate and acetic anhydride were used, crystalline 2-*deoxy*-β-D-*glucose* 1 : 3 : 4 : 6-*tetra-acetate* was obtained.

According to Green and Pacsu (*J. Amer. Chem. Soc.*, 1937, **59**, 1205) it is possible to prepare an alkylfuranoside of a sugar by treating a mercaptal of the sugar with mercuric chloride, yellow mercuric oxide, and the appropriate alcohol. The reaction proceeds in two stages, *e. g.* :



Reaction 1 Reaction 2

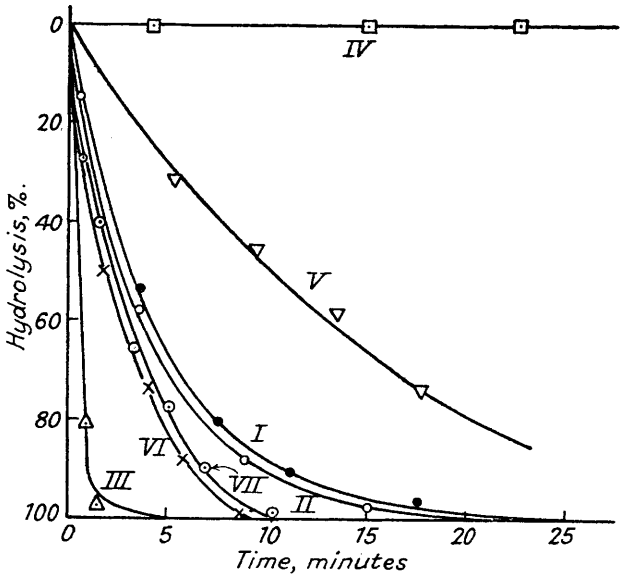
and a thioglycofuranoside is formed as an intermediate. If reaction 2 proceeds much faster than reaction 1, the intermediate cannot be isolated. Thus, Green and Pacsu (*loc. cit.*) were unable to isolate an intermediate compound in the conversion of galactose diethyl mercaptal into ethylgalactofuranoside. In the glucose series however, the corresponding intermediate compound was isolated. In view of the finding described below that the 2-deoxy-group greatly increased the lability of a glycosidic group on $C_{(1)}$, we thought it of interest to determine whether it was possible to isolate a thioglycoside of 2-deoxyglucofuranose or whether the presence of the deoxy-group on $C_{(2)}$ of the sugar would make the glycoside so labile that its isolation would be improbable. The latter proved to be the case, for treatment of 2-deoxyglucose dibenzyl mercaptal under the appropriate conditions for obtaining the intermediate compound yielded only 2-deoxyglucopyranose and unchanged 2-deoxyglucose dibenzyl mercaptal, indicating that some initial material had been completely demercaptalated with subsequent exhaustion of the mercuric chloride and cessation of any further reaction. When dry methanol was added during the demercaptalation of 2-deoxyglucose dibenzyl mercaptal, there was obtained a methyl-2-deoxyglucoside; we regard this as being a *methyl-2-deoxyglucofuranoside*, since it differed from the already known α- and β-methyl-2-deoxyglucopyranosides and moreover its rate of oxidation with lead tetra-acetate was much more rapid than that of αβ-methyl-2-deoxyglucopyranoside. This behaviour is indicative of the presence of *cis*-hydroxyl groups in the sugar and hence of a furanose structure.

Furthermore its rate of hydrolysis with 0·005N-hydrochloric acid was of the same order as the corresponding rate of hydrolysis of αβ-methyl-2-deoxy-D-glucofuranoside (cf. Hughes, Overend, and Stacey, following paper) and differed from that of α-methyl-2-deoxy-D-glucopyranoside.

A comparative measurement of the rates of hydrolysis of methyl-furano- and -pyrano-glycosides of 2-deoxy-D-glucose and 2-deoxy-D-ribose indicated that the furanose form was hydrolysed exceedingly rapidly and that both glycosidic types were hydrolysed much more rapidly than the corresponding normal sugar derivatives (see figure). The extent of hydrolysis was followed polarimetrically and it will be seen that α-methyl-2-deoxy-D-glucopyranoside was hydrolysed to some extent by 0·05N-hydrochloric acid whereas β-methyl-D-glucoside showed no change in optical rotation when treated with N-hydrochloric acid. αβ-Methyl-2-deoxy-D-glucofuranoside on the other hand was completely hydrolysed in 10 minutes by 0·005N-hydrochloric

acid at 15°. Similarly αβ-methyl-2-deoxy-L-ribofuranoside was hydrolysed much more rapidly by 0·005N-hydrochloric acid at 100° than was either α- or β-methyl-2-deoxy-L-ribopyranoside.

Calculation, from the experimental data, of the velocity constant for hydrolysis of α- and β-methyl-2-deoxy-L-ribopyranoside to 2-deoxy-L-ribose gave a value of 0·101. This value may be compared with the velocity constant (0·0068) for the hydrolysis of α-methyl-D-arabinofuranoside in 0·01N-hydrochloric acid (Montgomery and Hudson, *J. Amer. Chem. Soc.*, 1937, **59**, 992); the deoxy-sugar derivatives are much more rapidly hydrolysed. Moreover the hydrolysis of α- and β-methyl-D-arabinopyranoside requires a considerably higher concentration of acid, and the value of the velocity constant for the hydrolysis of α-methyl-D-arabinofuranoside is approximately 10 times that for α- and β-methyl-D-arabinopyranoside calculated in terms of the same acid concentration (*idem, ibid.*).



I. ● α-*Methyl-2-deoxy-*L-*ribopyranoside* (0·005N-HCl *at* 100°).
II. ○ β-*Methyl-2-deoxy-*L-*ribopyranoside* (0·005N-HCl *at* 100°).
III. △ αβ-*Methyl-2-deoxy-*L-*ribofuranoside* (0·005N-HCl *at* 100°).
IV. ⊡ β-*Methyl-*D-*glucopyranoside* (1N-HCl *at* 17°).
V. ▽ α-*Methyl-2-deoxy-*D-*glucopyranoside* (0·05N-HCl *at* 15°).
VI. × αβ-*Methyl-2-deoxy-*D-*glucofuranoside* (0·005N-HCl *at* 15°).
VII. ⊙ αβ-*Methyl-2-deoxy-*D-*glucoside obtained from the mercaptal derivative* (0·005N-HCl *at* 15°).

It seems that in 2-deoxy-sugars the methylene group greatly increases the lability of the glycoside group at $C_{(1)}$, and this effect is enhanced when the ring structure is of the furanose type.

Experimental.

D-*Glucal.*—Triacetyl glucal (5·86 g.) was dissolved in dry methanol (100 c.c.), and sodium (15 mg.) was added. The solution was kept at room temperature overnight and then evaporated to a dry residue which was extracted once with a very small amount of water. The residue was then thoroughly dried. The crystals (hygroscopic) recrystallised from ethyl acetate in absence of moisture as colourless needles (3·0 g.), m. p. 58—60°, $[\alpha]_D^{22}$ −7° (*c*, 1·47 in water).

2-*Deoxy-*D-*glucose.*—Glucal (10·5 g.) in ice-cold 2N-sulphuric acid (100 c.c.) was kept overnight at 0°. After filtration the solution was stirred with charcoal and then neutralised with barium hydroxide and barium carbonate. The filtered solution was evaporated to dryness under diminished pressure. Trituration of the syrupy residue with dry acetone separated the product into crystals of 2-deoxy-D-glucose (4·63 g.) and a syrupy residue (*A*). The crystals were recrystallised several times from aqueous ethanol and acetone, m. p. 146°, $[\alpha]_D^{17\cdot5}$ +38·3° ⟶ + 45·9° in 35 minutes (*c*, 0·52 in water); $[\alpha]_D^{17\cdot5}$ +22·8° ⟶ +80·8° in 24 hours (*c*, 0·57 in pyridine). Bergmann *et al.* (*Ber.*, 1921, **54**, 453; 1922, **55**, 158) give m. p. 148° and $[\alpha]_D^{19}$ +46·6° (in water) and $[\alpha]_D^{18}$ +15·2° ⟶ + 90·2° in 20 hours (in pyridine). Fischer and Sowden (*J. Amer. Chem. Soc.*, 1947, **69**, 1048) report m. p. 128—129° and $[\alpha]_D^{23}$ +46·6° at equilibrium after 1 hour (in water) (Found: C, 43·3; H, 7·5. Calc. for $C_6H_{12}O_5$: C, 43·9; H, 7·3%).

2-*Deoxy-*D-*glucose Anilide* (with K. Butler).—2-Deoxy-D-glucose (0·1 g.), suspended in absolute ethanol (12 c.c.), was boiled for 1½ hours with aniline (0·1 g.). No reaction was apparent, and conse-

quently water (1 c.c.) was added and the mixture was boiled for a further ½ hour. A slight brown residue was removed by filtration, and on being kept the filtrate deposited 2-*deoxy*-D-*glucose anilide* (0·090 g.) which recrystallised from ethanol in the form of colourless needles, m. p. 193—194°, $[\alpha]_D^{20}$ −138° ⟶ − 106° (2 days) (*c*, 1·0 in pyridine) (Found : C, 60·3; H, 7·1; N, 5·6. $C_{12}H_{17}O_4N$ requires C, 60·2; H, 7·1; N, 5·8%).

Regeneration of 2-Deoxyglucose from its Anilide.—2-Deoxy-D-glucose anilide (80 mg.) was treated with 0·5% formic acid (20 c.c.) for 1 hour at 80°. The excess of formic acid and aniline were then removed by steam-distillation, and the solution was neutralised with lead carbonate. The filtered liquor was concentrated to dryness, and the residue dissolved in 95% alcohol. The lead was removed from solution by means of hydrogen sulphide and, after decolorisation with charcoal, the solvent was removed by evaporation and a light-yellow coloured syrup remained. This, on nucleation with 2-deoxy-D-glucose, slowly crystallised. These crystals (0·0134 g.) had m. p. 142° alone and in admixture with 2-deoxy-D-glucose; $[\alpha]_D^{17}$ +46° [equilibrium value in water (*c*, 1·0)].

Acetylation of 2-Deoxy-D-glucose.—(*a*) 2-Deoxy-D-glucose (0·15 g.) was suspended in dry pyridine (2·5 c.c.) at 0°, and freshly distilled acetic anhydride (2 c.c.) was added. The reaction mixture was kept at 0° for 3 days, at the end of which time the 2-deoxyglucose had completely dissolved. The solution was diluted with water and then extracted with chloroform. The extract was washed with 0·01N-sulphuric acid, dilute sodium hydrogen carbonate solution, and finally with water. After drying ($CaCl_2$) the solvent was removed by evaporation, and the residue was evaporated several times with absolute ethanol. The oily residue crystallised after trituration with ethanol–ether. After recrystallisation from ethanol, *tetra-acetyl* α-2-*deoxy*-D-*glucose*, m. p. 91°, $[\alpha]_D^{20}$ +12·30° (*c*, 0·325 in ethanol) (Found : C, 50·4; H, 6·3. $C_{14}H_{20}O_9$ requires C, 50·6; H, 6·1%), was obtained.

(*b*) 2-Deoxy-D-glucose (0·1 g.), acetic anhydride (0·5 g.), and fused sodium acetate (0·1 g.) were heated together under reflux for 30 minutes. After cooling the mixture was diluted with water, and the resulting solution was extracted with chloroform. The extract was dried ($MgSO_4$) and the solvent was removed by evaporation. The residue was evaporated several times with absolute ethanol and then dried. A colourless oil remained, having n_D^{20} 1·4555. After several months the oil crystallised and recrystallised from ethanol–water in colourless cubes. It was *tetra-acetyl* β-2-*deoxy*-D-*glucose*, m. p. 75—78°, $[\alpha]_D^{20}$ +30° (*c*, 0·20 in ethanol) (Found : C, 50·8; H, 6·4. $C_{14}H_{20}O_9$ requires C, 50·6; H, 6·1%).

2-*Deoxy*-D-*glucose Dibenzyl Mercaptal.*—2-Deoxy-D-glucose (1·4 g.) and toluene-ω-thiol (2·5 g.) were mixed. Concentrated hydrochloric acid (5 c.c.) was added and the reaction mixture was shaken vigorously for 30 minutes. After about 15 minutes the mixture became semi-solid. It was diluted with chloroform and then poured on ice. At the water–chloroform interface crystals separated; they were collected by filtration. The chloroform layer was separated and the aqueous layer was extracted with chloroform. The chloroform layer and extract were combined and evaporated, giving a small amount of crystalline material. The total crop of crystals obtained recrystallised from ethanol or methanol as colourless needles of 2-*deoxy*-D-*glucose dibenzyl mercaptal*, m. p. 154°, $[\alpha]_D^{19}$ −40° (*c*, 0·6 in ethanol), which were slightly soluble in cold ethanol and acetone and insoluble in water (Found : C, 61·0; H, 6·6; S, 15·8. $C_{20}H_{26}O_4S_2$ requires C, 60·9; H, 6·6; S, 16·2%).

Demercaptalation of 2-Deoxyglucose Dibenzyl Mercaptal.—2-Deoxyglucose dibenzyl mercaptal (0·3 g.) was dissolved in boiling acetone (10 c.c.) and water (5 c.c.). Mercuric chloride and yellow mercuric oxide were added and the reaction mixture was boiled for 15 minutes. The insoluble mercury compounds were filtered off and pyridine (3 c.c.) was added to the filtrate. The solution was kept at 0° overnight. The crystalline mercuric chloride–pyridine addition compound which separated was removed by filtration, and the filtrate was evaporated to dryness. A syrupy residue remained which solidified (0·075 g.) when nucleated with 2-deoxyglucose. After recrystallisation from aqueous alcohol–acetone it had m. p. 145—146° alone or in admixture with 2-deoxyglucose.

Purification of Syrupy 2-Deoxy-D-glucose.—The syrupy 2-deoxy-D-glucose (*A*) (p. 2843) (5·1 g.) remaining after the crystallisation of the sugar was mixed with toluene-ω-thiol (8 g.). Concentrated hydrochloric acid (12 c.c.) containing zinc chloride (6 g.) was added to the reaction mixture which was vigorously shaken for 30 minutes. After about 15 minutes solid began to separate. The reaction mixture was diluted with water (250 c.c.). The brown solid which separated was collected by filtration and recrystallised (2·49 g.) from ethanol; m. p. 154° alone or in admixture with 2-deoxy-D-glucose dibenzyl mercaptal.

Demercaptalation of this 2-deoxy-D-glucose dibenzyl mercaptal (2·49 g.) by the method described yielded 2-deoxy-D-glucose (0·67 g., 65·5%), which after recrystallisation from aqueous ethanol–acetone had m. p. 145—146° and $[\alpha]_D^{16}$ +45·4° (equilibrium) (*c*, 0·52 in water).

Attempted Preparation of Benzylthio-α-2-deoxyglucofuranoside.—(*a*) 2-Deoxyglucose dibenzyl mercaptal (1·0 g.) was dissolved in aqueous ethanol (10 c.c.), and mercuric chloride (0·25 mol., 0·17 g.) and yellow mercuric oxide (1 g.) were added. The reaction mixture was shaken overnight at room temperature. Insoluble mercury compounds were removed by filtration, and the mercuric chloride in the filtrate was removed in the usual manner by adding pyridine. After the mercuric chloride–pyridine addition complex had been filtered off, the filtrate was evaporated to dryness. Fractional crystallisation of the residue yielded benzylthiomercuric chloride ($C_6H_5{\cdot}CH_2{\cdot}S{\cdot}HgCl$), 2-deoxyglucose (0·15 g.), m. p. 145—146°, and unchanged 2-deoxyglucose dibenzyl mercaptal (0·5 g.), m. p. 154°. Extraction with hot acetone of the insoluble mercury compounds and evaporation of the extract to dryness also afforded some unchanged 2-deoxyglucose dibenzyl mercaptal (0·1 g.).

(*b*) 2-Deoxyglucose dibenzyl mercaptal (0·67 g.), mercuric chloride (0·66 mol., 0·30 g.) and yellow mercuric oxide (1 g.) were suspended in 10% aqueous ethanol (7·5 c.c.). The reaction was followed as above, but only unchanged 2-deoxyglucose dibenzyl mercaptal (0·40 g.), m. p. 154°, and 2-deoxyglucose (0·10 g.), m. p. 145—146°, $[\alpha]_D^{16}$ +45·9° (equilibrium) (*c*, 0·326 in water), were isolated.

Methy-2-deoxy-D-*glucofuranoside.*—2-Deoxyglucose dibenzyl mercaptal (0·5 g.), mercuric chloride (1·2 g.), and yellow mercuric oxide (2·0 g.) were suspended in dry methanol (100 c.c.). The suspension was mechanically agitated for 6 hours at room temperature. The insoluble mercuric compounds were filtered off and washed with warm methanol. The washings were added to the filtrate, and then pyridine

(10 c.c.) was added to the mixture. The solution was kept at 0° overnight. The pyridine–mercuric chloride complex which separated was removed by filtration, and the filtrate was evaporated to dryness under diminished pressure. The residue was dissolved in water, and the solution filtered and then again evaporated. The residue was extracted with methanol, removal of which yielded a colourless syrup—*methyl-2-deoxy-*D*-glucofuranoside*, n_D^{19} 1·4931, $[\alpha]_D^{20}$ +69·5° (*c*, 0·23 in ethyl alcohol) (Found: OMe, 16·8. $C_7H_{14}O_5$ requires OMe, 17·4%). Cf. *β*-methyl-2-deoxy-D-glucopyranoside, m. p. 122°, $[\alpha]_D^{20}$ −48·4°, and *α*-methyl-2-deoxy-D-glucopyranoside, m. p. 91°, $[\alpha]_D^{20}$ +137·9° (Fischer, Bergmann, and Schotte, *Ber.*, 1920, **53**, 545; Bergmann, *Annalen*, 1925, **443**, 223; Bergmann, Schotte, and Lechinsky, *Ber.*, 1922, **55**, 158). The methyl-2-deoxy-D-glucofuranoside (0·3 g.) was oxidised with a solution of lead tetra-acetate in dry benzene. The reaction was followed iodometrically. One mole of the tetra-acetate was consumed. A comparative experiment with *αβ*-methyl-2-deoxy-D-glucopyranoside showed that this substance also consumed one mole of lead tetra-acetate, but the rate of its oxidation was much slower.

3 : 4 : 5 : 6-*Tetra-acetyl* 2-*Deoxy-*D*-glucose Dibenzyl Mercaptal.*—2-Deoxy-D-glucose dibenzyl mercaptal (0·3 g.) was dissolved in dry pyridine (2·5 c.c.), and the solution was cooled to 0°. Freshly distilled acetic anhydride (1·5 g.) was added, and the solution was kept at 0° overnight and then poured into water (50 ml.). An oil separated which quickly solidified. It was collected by filtration and recrystallised from ethanol–water or methanol. Long colourless needles of the *acetylated dibenzyl mercaptal* (0·26 g.) were obtained, having m. p. 63° and $[\alpha]_D^{17}$ +18·2° (*c*, 0·77 in methanol) (Found: S, 11·3; OAc, 30·4. $C_{28}H_{34}O_8S_2$ requires S, 11·4; OAc, 30·6%).

Repetition of Fischer and Sowden's Method (loc. cit.) *of preparing* 2-*Deoxy-*D*-glucose.*—Treatment of D-arabinose (15 g.) with nitromethane and sodium methoxide, followed by acetylation, afforded 33·2% of 1-nitro-D-*arabo*-tetra-acetoxyhexene (12·0 g.; m. p. 115°). Reduction of this (10 g.) with hydrogen in the presence of a palladium catalyst yielded 7·5 g. (71%) of 1-nitro-1 : 2-dideoxy-D-*arabo*-hexitol tetra-acetate, m. p. 90—91°, $[\alpha]_D^{20}$ +29·6° (Fischer and Sowden give m. p. 115—116° and 91—92° respectively for these compounds).

The above substance (7·0 g.) was dissolved in N-NaOH (105 c.c.) and kept for 1 hour. It was then added to a stirred mixture of water (25 c.c.) and sulphuric acid (14·7 c.c.) at room temperature. The solution was diluted with water and neutralised (barium carbonate). The filtered solution was treated with a few drops of acetic acid and then evaporated under diminished pressure. The resulting syrup was redissolved in a small quantity of ethanol, filtered, and again concentrated to dryness; on being stored for some weeks in a vacuum, the syrup obtained slowly crystallised and was recrystallised (1·0 g.) from aqueous ethanol by addition of acetone. The 2-deoxy-D-glucose had m. p. 128—131° and repeated crystallisation tended slightly to lower this value. It was probably a mixture mainly in the *α*-form, since Fischer and Sowden (*loc. cit.*) report similar observations.

Rates of Hydrolysis Experiments.—(*a*) *α-Methyl-2-deoxy-*L*-ribopyranoside.* α-Methyl-2-deoxy-L-ribopyranoside (0·0352 g.) was dissolved in 0·005N-hydrochloric acid (5 c.c.), and the solution heated at 100°. The following polarimetric observations were obtained:

Time (minutes)	Initial	3·5	7·5	11·5	17·5	27·5
$[\alpha]_D^{20}$	−0·34°	+11°	+37°	+47°	+51°	+51°

After this time the solution strongly reduced Fehling's solution.

(*b*) *β-Methyl-2-deoxy-*L*-ribopyranoside.* A similar procedure with the *β*-derivative gave the following results:

Time (minutes)	Initial	4	9	15	25
$[\alpha]_D^{20}$	+190°	+112°	+66°	+49°	+49°

(*c*) *αβ-Methyl-2-deoxy-*L*-ribofuranoside.* This furanoside (0·1505 g.) was dissolved in 0·005N-hydrochloric acid (15 c.c.), and the rotation was observed ($[\alpha]_D$ −33°). The solution was rapidly heated to 100° and the optical rotation changed rapidly (3 minutes).

(*d*) *α-Methyl-2-deoxy-*D*-glucopyranoside.* The glucoside (0·25 g.) was hydrolysed with 0·05N-hydrochloric acid (35 c.c.) at 15° and the reaction was followed as before (initial value of $[\alpha]_D^{20}$ +130° and after 30 minutes the hydrolysis was incomplete).

(*e*) *αβ-Methyl-2-deoxy-*D*-glucofuranoside.* The hydrolysis of this compound (0·022 g.) was effected with 0·005N-hydrochloric acid (4 c.c.) at room temperature and was complete in about 8 minutes.

The micro-analyses were carried out partly by Dr. W. T. Chambers and partly by Drs. Weiler and Strauss. One of us (W. G. O.) thanks the British Rubber Producers' Research Association for financial assistance which enabled him to take part in this work. We also thank Messrs. Imperial Chemical Industries Ltd. for a grant in aid of this work.

THE UNIVERSITY, BIRMINGHAM 15. [*Received, February 28th*, 1949.]