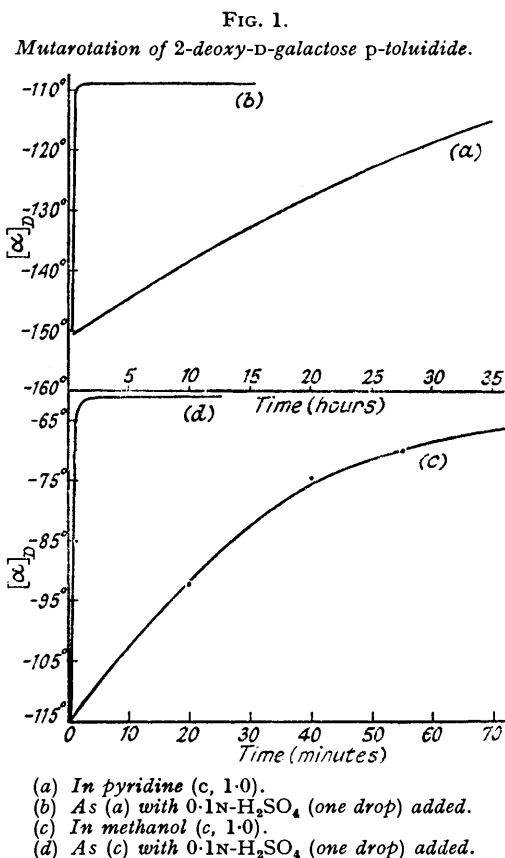


218. Deoxy-sugars. Part XIV. A Further Contribution to the Chemistry of 2-Deoxy-D-galactose.

By A. B. FOSTER, W. G. OVEREND, and M. STACEY.

A study of the properties and reactions of 2-deoxy-D-galactose has been extended (cf. *J.*, 1950, 671). Numerous new derivatives are described and compounds suitable as intermediates for the preparation of phosphoric acid derivatives of 2-deoxy-D-galactose have been prepared and their structures established. The action of ethanolic hydrogen chloride on the deoxyhexose has been investigated.

INVESTIGATIONS during recent years have shown, increasingly, that the rôle of sugar phosphates in biological processes is of great importance. For example, the phosphoric acid derivatives of D-ribose and its 2-deoxy-analogue form significant elements in the structure of nucleic acids. An understanding of the biological action of these macromolecules must involve a detailed study of their building units. We have already described some experiments of this nature



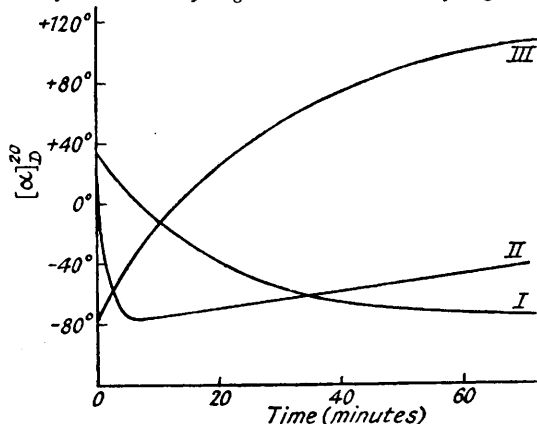
and, in this and the following two communications, the preparation and properties of phosphoric acid derivatives of some 2-deoxy-sugars are described. Because of its availability and the crystalline nature of its derivatives, 2-deoxy-D-galactose has again been used in these model reactions. Of the components of deoxyribonucleic acid, 2-deoxy-D-ribose-3 and -5 phosphoric acid are important members. Since in the former compound the hydroxyl group adjacent to the methylene group is esterified by phosphoric acid and in the latter it is the primary hydroxyl group which is esterified, we expect some differences in their chemical stabilities. With 2-deoxy-D-galactose the corresponding derivatives are the 3- and the 6-phosphoric acids.

This paper describes the preparation of derivatives of this 2-deoxyhexose suitably protected so that phosphorylation will afford the required 2-deoxy-D-galactose-3 and -6 phosphoric acids.

D-Galactal prepared by the usual reactions, when dissolved in cold 5% sulphuric acid, yielded 2-deoxy- β -D-galactose. It has recently been shown that trifluoroacetic acid can successfully replace sulphuric acid in such reactions as aromatic nitration (Bourne, Stacey, Tatlow, and Tedder, unpublished results). It has now been shown that trifluoroacetic acid can also be used to convert D-galactal into 2-deoxy- β -D-galactose, the deoxy-sugar being characterised as its *p*-toluidine derivative. It was found that mutarotation of this compound occurred slowly when dry methanol and dry pyridine were used as solvents. Addition of one drop of 0.1N-sulphuric acid resulted in rapid attainment of the mutarotational equilibrium. The changes are shown in Fig. 1 (cf. Butler, Laland, Overend, and Stacey, *J.*, 1950, 1433, for analogous work with the 2-deoxy-D-galactose anilide). The deoxy-sugar also formed a crystalline diethyl and dibenzyl mercaptal. Treatment of 2-deoxy-D-galactose diethyl mercaptal with acetone in the presence of anhydrous zinc chloride, syrupy phosphoric acid, and phosphoric oxide, afforded 3 : 4-5 : 6-diisopropylidene 2-deoxy-D-galactose diethyl mercaptal.

The action of methanolic hydrogen chloride on a 2-deoxyhexose was first studied in detail by Hughes, Overend, and Stacey (*J.*, 1949, 2846). It was shown that treatment of 2-deoxy-D-glucose with methanolic hydrogen chloride resulted in a series of characteristic changes in the

FIG. 2.
Action of methanolic hydrogen chloride on 2-deoxy-D-galactose.



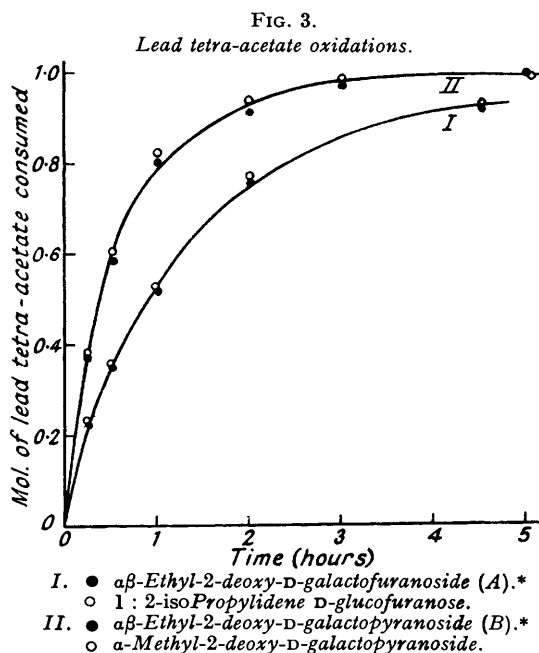
0.03% (I), 0.3% (II), and 3.0% (III) Methanolic hydrogen chloride.

optical rotation of the sugar. A similar series of changes has been revealed by the action of methanolic hydrogen chloride on 2-deoxy-D-galactose, but in this case the changes in optical rotation were found to be much greater than those observed with 2-deoxy-D-glucose. By using methanolic hydrogen chloride of various concentrations, a detailed examination of the whole range of changes in optical rotation was achieved (see Fig. 2). Treatment of 2-deoxy-D-galactose with 0.03% methanolic hydrogen chloride resulted in a decrease of the optical rotation to a minimum value of $-75^{\circ} \pm 2^{\circ}$. The difference between the initial and final (minimum) value was 112° (cf. 2-deoxy-D-glucose, for which the analogous figure was 4°). Termination of the reaction at the minimum value afforded a syrupy product which was shown by Overend, Shafizadeh, and Stacey (*J.*, 1950, 671) to be $\alpha\beta$ -methyl-2-deoxy-D-galactofuranoside. When 2-deoxy-D-galactose was treated with 0.3% methanolic hydrogen chloride, the minimum value of the optical rotation was rapidly attained and was followed by a slow increase. When 3% methanolic hydrogen chloride was used, the minimum value of the optical rotation was attained instantaneously and was followed by a rapid increase to a maximum value of $125^{\circ} \pm 2^{\circ}$. Termination of the reaction at this stage afforded crystalline α -methyl-2-deoxy-D-galactopyranoside (cf. Overend, Shafizadeh, and Stacey, *loc. cit.*). Treatment of α -methyl-2-deoxy-D-galactoside with acetic anhydride and pyridine yielded syrupy 3 : 4 : 6-triacetyl α -methyl-2-deoxy-D-galactoside.

A series of changes similar to those described have been observed on treatment of 2-deoxy-D-galactose with ethanolic hydrogen chloride. Treatment of the deoxy-sugar with 2% ethanolic hydrogen chloride resulted in a rapid fall in the optical rotation to a minimum value

of $-56^{\circ} \pm 2^{\circ}$. Termination of the reaction at this stage yielded syrupy $\alpha\beta$ -ethyl-2-deoxy-D-galactofuranoside. However, when the reaction was allowed to proceed until the optical rotation had reached a maximum value, the main product was $\alpha\beta$ -ethyl-2-deoxy-D-galactopyranoside. A study of the rates of oxidation of these glycosides by lead tetra-acetate (see Fig. 3) confirmed that they had been correctly designated. Moreover, it was shown that, when D-galactal, which is known to have a pyranose structure, was treated with ethanolic hydrogen chloride, it afforded a glycoside identical in properties with that described above as $\alpha\beta$ -ethyl-2-deoxy-D-galactopyranoside (cf. Overend, Shafizadeh, and Stacey, *loc. cit.*; Deriaz, Overend, Stacey, and Wiggins, *J.*, 1949, 2836).

When α -methyl-2-deoxy-D-galactoside was shaken with benzaldehyde containing anhydrous zinc chloride or heated in benzaldehyde at 145° in an atmosphere of carbon dioxide (Oldham and Honeyman, *J.*, 1946, 986), 4 : 6-benzylidene α -methyl-2-deoxy-D-galactoside (Tamm and Reichstein, *Helv. Chim. Acta*, 1948, **31**, 1630) was obtained in 56.4% and 14% yield respectively. This on treatment with toluene-*p*-sulphonyl chloride in pyridine gave a monotoluene-*p*-sulphonyl derivative which did not react with sodium iodide in hot anhydrous acetone. It



was 4 : 6-benzylidene 3-toluene-*p*-sulphonyl α -methyl-2-deoxy-D-galactoside since this failure to react confirmed that the toluene-*p*-sulphonyloxy-group was not located at position 6 of the sugar derivative. On treatment of α -methyl-2-deoxy-D-galactoside with acetone containing anhydrous zinc chloride 3 : 4-isopropylidene α -methyl-2-deoxy-D-galactoside was obtained. That the isopropylidene residue in this was located at C₍₃₎ : C₍₄₎ was indicated by the fact that on treatment of the isopropylidene derivative with toluene-*p*-sulphonyl chloride in pyridine a crystalline monotoluene-*p*-sulphonyl derivative was obtained. This on treatment with sodium iodide in dry acetone under standard conditions underwent 36% exchange, thereby indicating that the toluene-*p*-sulphonyloxy-group was formed by reaction of the primary hydroxyl group in the sugar derivative (*i.e.*, that at C₍₆₎). Consequently the monotoluene-*p*-sulphonyl derivative was 3 : 4-isopropylidene 6-toluene-*p*-sulphonyl α -methyl-2-deoxy-D-galactoside. The incomplete exchange is in agreement with results previously reported (Foster, Overend, Stacey, and Wiggins, *J.*, 1949, 2542). Attempts to remove the isopropylidene residue by anhydrous methanolic hydrogen chloride or aqueous methanolic hydrochloric acid led to a crystalline substance which rapidly decomposed to a resinous material and could not be identified.

4 : 6-Benzylidene and 3 : 4-isopropylidene α -methyl-2-deoxy-D-galactoside were suitable intermediates for preparing 2-deoxy-D-galactose-3 and -6 phosphoric acid respectively (see following communication).

* For interpretation of (A) and (B) see p. 978.

EXPERIMENTAL.

2-Deoxy- β -D-galactose.—(a) *By the action of sulphuric acid on D-galactal.* D-Galactal (30 g.) was dissolved in cold 5% sulphuric acid (400 c.c.), and the solution was kept at 0° for 24 hours, and then adjusted to pH 7 by addition of aqueous barium hydroxide. The barium residues were collected by filtration and well washed with water. The washings were added to the filtrate which was then evaporated under diminished pressure to a syrup. Methanol was distilled over the syrup several times to remove traces of water. The pale yellow syrup which was finally obtained was dissolved in dry methanol (50 c.c.), filtered through a carbon pad, and set aside. 2-Deoxy- β -D-galactose (14 g.) crystallised readily and a further crop of crystals (4 g.) was obtained after concentration of the mother-liquors. The deoxyhexose had m. p. 120—121°, and $[\alpha]_D^{20} + 8^\circ$ changing to $+38^\circ \pm 2^\circ$ after 70 minutes (*c.*, 2.0 in methanol), and $+24^\circ$ changing to $+56^\circ \pm 2^\circ$ after 120 minutes (*c.*, 2.0 in water). Pigman and Isbell (*J. Res. Nat. Bur. Stand.*, 1937, **19**, 189; 1939, **22**, 397) give m. p. 120—121°, and $[\alpha]_D^{20} + 40.8^\circ$ changing to $+60.5^\circ$ after 30 minutes in water; Overend, Shafizadeh, and Stacey (*J.*, 1950, 671) report $[\alpha]_D^{17} + 33.6^\circ$ after 2 minutes, changing to $+57^\circ$ after 46 minutes in water, and Tamm and Reichstein (*Helv. Chim. Acta*, 1948, **31**, 1630) quote $[\alpha]_D^{18} + 60.7^\circ$ in water.

(b) *By the action of trifluoroacetic acid on D-galactal.* D-Galactal (1.0 g.) was dissolved in water (13 c.c.) at 0° containing trifluoroacetic acid (1.0 g.), and the solution was set aside at 0° for 48 hours. The green and slightly turbid solution was filtered through a charcoal pad and evaporated in the frozen state. The syrupy residue was dissolved in the minimum volume of water, and adjusted to pH 7 by the addition of sodium carbonate. After being shaken with charcoal the solution was evaporated to a syrup and then crystallised as in (a) above. 2-Deoxy- β -D-galactose (0.52 g.; m. p. 120—121°) was obtained.

2-Deoxy-D-galactose p-Toluidide.—A solution of 2-deoxy- β -D-galactose (0.3 g.) in 95% ethanol (7 c.c.) was boiled under reflux with *p*-toluidine (0.23 g., 1.1 mols.) for 2 hours. After 24 hours at 0° crystals had separated and were collected. After recrystallisation from ethanol, 2-deoxy-D-galactose *p*-toluidide (0.25 g., 54%) was obtained as large colourless prisms, m. p. 142—143°, $[\alpha]_D^{20} - 148.9^\circ$ (*c.*, 0.8 in pyridine) (Found: C, 61.9; H, 7.6; N, 5.2. Calc. for C₁₃H₁₉O₄N: C, 61.7; H, 7.5; N, 5.5%). 2-Deoxy-D-galactose *p*-toluidide showed mutarotation in methanol and pyridine.

(a) Pyridine as solvent: The optical rotation of a 1% solution of the toluidide in dry pyridine changed from -150° after 1 minute to -115° after 72 hours. When 1 drop of 0.1N-sulphuric acid was added to a similar solution, the changes observed were -127.5° after 1 minute, altering to -110° after 9 minutes. (b) Methanol as solvent: The optical rotation of a 1% solution of the *p*-toluidide in dry methanol changed from -117° after 1 minute to -65° after 100 minutes. If 1 drop of 0.1N-sulphuric acid was added to a similar solution the changes observed in optical rotation were -115° (extrapolated initial value) to -62.5° after 3 minutes.

2-Deoxy-D-galactose Dibenzyl Mercaptal.—A solution of 2-deoxy- β -D-galactose (0.75 g.) in concentrated hydrochloric acid (1.5 c.c.) was shaken vigorously with toluene-*o*-thiol (2.6 mols., 1.3 c.c.). Treatment of the reaction mixture with ice and water gave a thick semi-solid mass which collapsed to a flocculent precipitate on treatment with ether. The solid was collected and washed alternately with water and ether. Recrystallisation from aqueous methanol gave 2-deoxy-D-galactose dibenzyl mercaptal (0.8 g., 44%) as glistening plates, m. p. 106—107°, $[\alpha]_D^{20} - 38^\circ$ (*c.*, 1.72 in pyridine) (Found: C, 61.2; H, 6.5; S, 15.6. C₂₀H₂₆O₄S₂ requires C, 60.9; H, 6.6; S, 16.2%).

2-Deoxy-D-galactose Diethyl Mercaptal.—On shaking of a solution of 2-deoxy- β -D-galactose (3 g.) in concentrated hydrochloric acid (6 c.c.) with ethanethiol (4.5 c.c.) for 2 hours at room temperature and then pouring of the reaction mixture into water, 2-deoxy-D-galactose diethyl mercaptal (4.3 g., 87%) was obtained. After recrystallisation from aqueous methanol the mercaptal showed m. p. 104—105° and $[\alpha]_D^{20} - 45^\circ$ (*c.*, 1.0 in ethanol). Overend, Shafizadeh, and Stacey (*loc. cit.*) record m. p. 104—105° for this compound.

3 : 4-5 : 6-Diisopropylidene 2-Deoxy-D-galactose Diethyl Mercaptal.—The diethyl mercaptal (4.2 g.) was shaken in dry acetone (150 c.c.) containing anhydrous zinc chloride (4 g.), phosphoric oxide (3 g.), and syrupy phosphoric acid (5 c.c.) at room temperature for 50 hours. The solution was poured into water containing an excess of sodium carbonate. The precipitated zinc salts were collected and well washed with acetone. The washings were added to the filtrate, which was then evaporated under diminished pressure to remove the acetone. The aqueous residue was extracted with chloroform (5 × 100 c.c.), the extract dried (MgSO₄), and the solvent removed by evaporation. Distillation of the syrupy residue afforded 3 : 4-5 : 6-diisopropylidene 2-deoxy-D-galactose diethyl mercaptal (3.5 g., 65%), b. p. 145—155° (bath-temp.)/0.05 mm., n_D^{20} 1.4835, $[\alpha]_D^{20} + 13.9^\circ$ (*c.*, 0.8 in acetone) (Found: C, 54.0; H, 8.2. C₁₆H₃₀O₄S₂ requires C, 54.8; H, 8.6%).

Treatment of 2-Deoxy-D-galactose Diethyl Mercaptal with Benzaldehyde.—(a) *In the presence of zinc chloride.* 2-Deoxy-D-galactose diethyl mercaptal (0.2 g.) was shaken with freshly distilled benzaldehyde (2 c.c.) and finally powdered anhydrous zinc chloride (1 g.). The mixture rapidly became deep red in colour and after 48 hours was treated with a mixture of water and light petroleum (b. p. 60—80°). No crystalline products could be isolated.

(b) *At elevated temperatures* (cf. Oldham and Honeyman, *J.*, 1946, 986). A mixture of freshly distilled benzaldehyde (3 c.c.) and 2-deoxy-D-galactose diethyl mercaptal (8 c.c.) was heated at 140—145° for 2 hours. A rapid stream of carbon dioxide was passed through the reaction mixture during this period. Working up in the usual manner gave no crystalline product.

Action of Methanolic Hydrogen Chloride on 2-Deoxy- β -D-galactose.—(a) 0.03% Methanolic hydrogen chloride. 2-Deoxy- β -D-galactose (0.1 g.) dissolved in dry methanol (9 c.c.) was allowed to mutarotate

to equilibrium (40 minutes). 0.3% Methanolic hydrogen chloride (1 c.c.) was added and the change in optical rotation observed :

Time (mins.)	4	8	13	19	30	40	70	90
$[\alpha]_D^{18}$	+17°	-3°	-21°	-37°	-52°	-63°	-73°	-75°

Neutralisation of the acid with excess silver carbonate after 90 minutes followed by removal of the silver residues and evaporation of the solvent gave a syrup which did not reduce Fehling's solution. It was $\alpha\beta$ -methyl-2-deoxy-D-galactofuranoside (cf. Overend, Shafizadeh, and Stacey, *loc. cit.*).

(b) 0.3% *Methanolic hydrogen chloride*. 3% Methanolic hydrogen chloride (1 c.c.) was added to a solution of 2-deoxy- β -D-galactose (0.1 g.) in dry methanol (9 c.c.), which had mutarotated to equilibrium. The changes observed in the optical rotation were as follows :

Time (mins.)	1	1.5	2.5	5	16	28	41	55	71
$[\alpha]_D^{18}$	-50°	-60°	-70°	-75°	-70°	-65°	-57°	-49°	-40°

(c) 3.0% *Methanolic hydrogen chloride*. Addition of 30% methanolic hydrogen chloride (1 c.c.) to a solution of 2-deoxy- β -D-galactose in methanol, identical with that previously described, resulted in the following changes in optical rotation :

Time (mins.)	0.5	1	5	11	16	25	40	90	200
$[\alpha]_D^{20}$	-77°	-60°	-43°	-14°	+11°	+43°	+74°	+106°	+114°

Neutralisation of the solution at the maximum value of the optical rotation and isolation of the product in the usual manner afforded α -methyl-2-deoxy-D-galactopyranoside, m. p. 112—113° after recrystallisation from ethyl acetate, $[\alpha]_D^{20} +155^\circ$ (c, 1.0 in water). Overend, Shafizadeh, and Stacey (*loc. cit.*) cite m. p. 112—113° for this compound, and Tamm and Reichstein (*loc. cit.*) give m. p. 109—110°.

3 : 4 : 6-*Triacetyl α -Methyl-2-deoxy-D-galactoside*.— α -Methyl-2-deoxy-D-galactoside (0.5 g.) in solution in dry pyridine (4 c.c.) was treated with excess of acetic anhydride for 4 days at room temperature. The reaction mixture was diluted with water (150 c.c.) and extracted with chloroform (3 \times 50 c.c.). The extract was washed successively with water, dilute aqueous sodium hydrogen carbonate, and again with water. After drying (MgSO₄) the solution was evaporated and afforded a straw-coloured syrup. On distillation 3 : 4 : 6-*triacetyl α -methyl-2-deoxy-D-galactoside* was obtained as a colourless syrup, b. p. 125—130° (bath-temp.)/0.03 mm., n_D^{20} 1.4504, $[\alpha]_D^{20} +159^\circ$ (c, 1.0 in benzene) (Found : C, 52.0; H, 7.2. C₁₃H₂₀O₈ requires C, 51.3; H, 6.7%).

Action of Ethanolic Hydrogen Chloride on 2-Deoxy- β -D-galactose.—(a) 0.8% *Ethanolic hydrogen chloride*. 2-Deoxy- β -D-galactose (0.1 g.) was dissolved in dry ethanol (5 c.c.) and allowed to mutarotate to equilibrium (40 minutes). 20.8% Ethanolic hydrogen chloride (0.2 c.c.) was then added and the changes in optical rotation of the solution were observed :

Time (mins.)	0	1	2	3	5	10	30
$[\alpha]_D^{18}$	+23°	-28°	-51°	-55°	-56°	-52°	-38°

In a parallel experiment the solution was neutralised after 5 minutes (*i.e.*, minimum value of the optical rotation) with excess of silver carbonate. Removal of the silver residues and evaporation of the solvent gave $\alpha\beta$ -ethyl-2-deoxy-D-galactofuranoside (A) as a colourless syrup, $[\alpha]_D^{20} -56^\circ$ in ethanol (Found : OEt, 23.0. C₈H₁₆O₅ requires OEt, 23.4%).

(b) 2.3% *Ethanolic hydrogen chloride*. A solution of 2-deoxy- β -D-galactose similar to that described above was treated with 20% ethanolic hydrogen chloride (0.7 c.c.), and the changes in optical rotation were observed polarimetrically :

Time (mins.)	0	1	2	6	12	27	43	800
$[\alpha]_D^{18}$	+22°	-46°	-42°	-30°	-10°	+24°	+42°	+101°

After 800 minutes the solution was neutralised and the product isolated in the usual manner. $\alpha\beta$ -Ethyl-2-deoxy-D-galactopyranoside (B) was obtained, having $[\alpha]_D^{20} +110^\circ$ in ethanol (Found : OEt, 22.9%).

Oxidation of (A) and (B) with Lead Tetra-acetate.—The oxidations were carried out according to the procedure of Hockett and McClenahan (*J. Amer. Chem. Soc.*, 1939, **61**, 1667) (cf. Overend, Shafizadeh, and Stacey, *loc. cit.*, for analogous experiments with the corresponding methylglycosides of 2-deoxy-D-galactose). The results obtained were as follows :

(a) $\alpha\beta$ -Ethyl 2-deoxy-D-galactofuranoside (96 mg.)

Time (hours)	0.25	0.5	1.0	2.0	4.5	80
Mols. of Pb(OAc) ₄ used	0.23	0.35	0.52	0.77	0.93	0.97

(b) $\alpha\beta$ -Ethyl 2-deoxy-D-galactopyranoside (95 mg.)

Time (hours)	0.25	0.5	1.0	2.0	3.0	5.0
Mols. of Pb(OAc) ₄ used	0.38	0.59	0.81	0.92	0.98	1.04

For purposes of comparison, a similar experiment was carried out on equimolecular amounts of 1 : 2-isopropylidene D-glucufuranose and α -methyl-2-deoxy-D-galactoside.

(c) 1 : 2-isopropylidene D-glucufuranose (110 mg.)

Time (hours)	0.25	0.5	1.0	2.0	2.5	4.5	8.0	15
Mols. of Pb(OAc) ₄ used ...	0.25	0.36	0.53	0.79	0.84	0.96	0.98	1.01

(d) α -Methyl 2-deoxy-D-galactoside (92 mg.)

Time (hours)	0.25	0.5	1.0	2.0	3.0	5.0
Mols. of Pb(OAc) ₄ used	0.39	0.61	0.83	0.94	1.0	1.07

Reaction of D-Galactal with Hydrogen Chloride in Primary Alcohols.—(a) 0.4% Methanolic hydrogen chloride. D-Galactal (0.1 g.) was dissolved in dry methanol (5 c.c.) ($[\alpha]_D^{20}$ of this solution was -29°), and 2.6% methanolic hydrogen chloride (1 c.c.) was added. The following changes in the optical rotation of the solution were observed polarimetrically:

Time (mins.)	1	2	3	5	9	14	20	43
$[\alpha]_D^{20}$	+6°	+58°	+80°	+102°	+116°	+122°	+125°	+127°

Neutralisation of the solution with silver carbonate and isolation of the product in the usual manner afforded α -methyl-2-deoxy-D-galactoside (60%), m. p. 112—113° alone or on admixture with the sample previously described.

(b) 0.8% Ethanolic hydrogen chloride. To a solution of D-galactal (0.1 g.) in ethanol (5 c.c.) ($[\alpha]_D^{20}$ -38° for this solution), 20% ethanolic hydrogen chloride (0.2 c.c.) was added and the changes in optical rotation were observed polarimetrically:

Time (mins.)	1	2	4	6	8	15	30	50
$[\alpha]_D^{20}$	+16°	+48°	+79°	+94°	+101°	+111°	+113°	+114°

Neutralisation of the solution and isolation of the product in the usual manner afforded $\alpha\beta$ -ethyl-2-deoxy-D-galactopyranoside, $[\alpha]_D^{20}$ +114° in ethanol (Found: OEt, 22.9%).

4: 6-Benzylidene α -Methyl-2-deoxy-D-galactoside.—(a) α -Methyl-2-deoxy-D-galactoside (4.7 g.) was shaken with freshly distilled benzaldehyde (15 c.c.) until dissolution was essentially complete. Finely powdered anhydrous zinc chloride (6 g.) was then added and the mixture was mechanically agitated for 3 days at room temperature. Addition of the mixture to water and light petroleum (b. p. 60—80°) afforded a crystalline solid. This was separated and dissolved in chloroform, and the solution washed successively with water, dilute aqueous sodium hydroxide solution, and again with water. After drying ($MgSO_4$) the solvent was removed by evaporation and the crystalline residue recrystallised from aqueous methanol. 4: 6-Benzylidene α -methyl-2-deoxy-D-galactoside (3.95 g., 56%) was obtained as colourless needles, m. p. 178—179°, $[\alpha]_D^{20}$ +106° (c, 0.62 in chloroform) (Found: C, 63.0; H, 6.6. $C_{14}H_{18}O_6$ requires C, 63.2; H, 6.8%) [Tamm and Reichstein, *loc. cit.* who described this compound after the completion of this work give m. p. 179—180° and $[\alpha]_D^{20}$ +108.4° \pm 3° (in chloroform)].

(b) (cf. Oldham and Honeyman, *loc. cit.*). α -Methyl-2-deoxy-D-galactoside (2.5 g.) and benzaldehyde (15 c.c.) were heated together at 140—145° for 2 hours, during which a stream of carbon dioxide was bubbled through the reaction mixture. After cooling, light petroleum (b. p. 60—80°) was added and unchanged material and its benzylidene derivative were separated as a semi-solid mass. After trituration with more light petroleum (b. p. 60—80°) this was dissolved in chloroform, and the product (0.5 g.) was isolated as described above, m. p. 178—179°.

4: 6-Benzylidene 3-Toluene-*p*-sulphonyl α -Methyl-2-deoxy-D-galactoside.—The benzylidene derivative (0.5 g.) was dissolved in dry pyridine (2 c.c.), and toluene-*p*-sulphonyl chloride (1.2 mols., 1.4 g.) was added. After 1 day at room temperature the reaction mixture was poured into water. The solid product was filtered off and recrystallised from ethanol. The toluene-*p*-sulphonyl derivative was obtained as colourless, lustrous plates, m. p. 134—135°, $[\alpha]_D^{20}$ +154.3° (c, 1.1 in chloroform) (Found: C, 59.8; H, 6.2. Calc. for $C_{21}H_{24}O_7S$: C, 60.0; H, 5.7%). The yield was quantitative (cf. Tamm and Reichstein, *loc. cit.*, who give m. p. 125—129° for this compound). When this compound (0.2 g.) was heated at 110—115° for 5 hours with excess of dry sodium iodide (0.5 g.) in dry acetone solution (5 c.c.), no reaction occurred and the starting materials could be recovered unchanged.

3: 4-isoPropylidene α -Methyl-2-deoxy-D-galactoside.— α -Methyl-2-deoxy-D-galactoside (2.3 g.) was shaken with dry acetone (50 c.c.) containing anhydrous zinc chloride (6 g.) at room temperature for 40 hours. The mixture was then poured into water (250 c.c.) containing an excess of sodium carbonate, and the precipitate was collected and washed with acetone. The washings were added to the filtrate which was evaporated under diminished pressure to small bulk. The aqueous residue was extracted exhaustively with chloroform, the extract was dried ($MgSO_4$), and the solvent evaporated. 3: 4-isoPropylidene α -methyl-2-deoxy-D-galactoside (1.0 g.) was obtained as a straw-coloured syrup, n_D^{20} 1.4660, $[\alpha]_D^{20}$ +92.5° (c, 1.04 in acetone) (Found: C, 54.8; H, 8.3. $C_{10}H_{18}O_5$ requires C, 55.0; H, 8.3%).

3: 4-isoPropylidene 6-Toluene-*p*-sulphonyl α -Methyl-2-deoxy-D-galactoside.—The isopropylidene derivative (0.66 g.) was dissolved in dry pyridine (4 c.c.), and toluene-*p*-sulphonyl chloride (0.7 g.) was added. After 20 hours at room temperature the product was isolated in the usual manner. After recrystallisation from aqueous ethanol, 3: 4-isoPropylidene 6-toluene-*p*-sulphonyl α -methyl-2-deoxy-D-galactoside (0.7 g.) was obtained as colourless prisms, m. p. 92—93°, $[\alpha]_D^{20}$ +44° (c, 0.91 in acetone) (Found: C, 54.9; H, 6.5; S, 8.7. $C_{17}H_{24}O_7S$ requires C, 54.8; H, 6.5; S, 8.6%). This compound (0.4 g.) was treated with anhydrous sodium iodide (0.19 g.) in dry acetone (10 c.c.) at 140° for 5 hours. Sodium toluene-*p*-sulphonate (82 mg.) was precipitated, corresponding to 36% of that required for complete exchange (cf. Foster *et al.*, *loc. cit.*).

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