56. *Fluorocarbohydrates. Part III.* Reactions of 6-Deoxy-6-fluoro-D-galactose.*

By P. W. Kent, A. Morris, and N. F. Taylor.

Reaction of 1,2:3,4-di-*O*-isopropylidene-6-*O*-methanesulphonyl-D-galactose with potassium fluoride in methanol leads to a mixture of the corresponding 6-deoxy-6-fluoro- and 6-*O*-methyl derivatives. Methanolysis of the product gives an isomorphous mixture of methyl 6-*O*-methyl-α-D-galactoside and the corresponding 6-fluoro-galactoside in the proportion of 2 : 1. Aqueous-acidic hydrolysis of these mixed products gives reducing sugars which are separable by paper chromatography. Methyl 6-deoxy-6-fluoro-α-D-galactoside is readily methylated with methyl iodide and silver oxide to a crystalline tri-*O*-methylglycoside which is converted by acidic hydrolysis into the corresponding free sugar and thence by oxidation with bromine into the 1,5-lactone. In these reactions the fluoro-sugar behaves normally and is not dehalogenated. Results indicate that this sugar is not readily defluorinated by mild catalytic or electrolytic reduction, though under vigorous conditions D-fucose is obtained. The α-glycoside of the fluoro-sugar is hydrolysed less readily than its unfluorinated analogue. The fluoro-sugar mutarotates at a rate very similar to that of the normal sugar.

In an earlier investigation[1] primary fluoro-sugars were synthesized by exchange of the corresponding methanesulphonic esters with potassium fluoride in ethanediol. Reaction in methanol gave products which contained both fluorine and methoxy-groups in non-stoicheiometrical amounts. Thus 1,2:3,4-di-*O*-isopropylidene-6-*O*-methanesulphonyl-D-galactose (I) furnished a di-isopropylidene product (II) which contained 7·8—8·2% of methoxyl and about 5% of fluorine and had constant physical properties (boiling point, refractive index) after repeated fractionations by vacuum-distillation. Furthermore, methanolysis of the product (II) gave, *inter alia*, a crystalline " methyl fluorogalactoside A " (III) containing non-stoicheiometrical amounts of fluorine and methoxyl (22·4%). This substance formed a tri-*O*-methanesulphonyl derivative (V) and consumed 2 mols. of sodium metaperiodate with liberation of one mol. of formic acid. It is clear, therefore, that in the " compound," three hydroxyl groups are present on contiguous carbon atoms. Molecular-weight determination on the product (II) precluded the possibility of dimerization. It is considered that these results can be attributed to the formation of a mixture of a 6-deoxy-6-fluoro- and a 6-*O*-methyl derivative. This view is substantiated by the following evidence: (i) Hydrolysis of the product (II) with aqueous mineral acid yielded a mixture of reducing sugars, indistinguishable by paper chromatography from 6-*O*-methyl- and 6-deoxy-6-fluoro-D-galactoses, and from which 6-*O*-methyl-D-galactose[2] was obtained crystalline. (ii) Methylation, by Purdie's reagents, of the products of methanolysis gives crystalline methyl 6-deoxy-6-fluoro-2,3,4-tri-*O*-methyl-α-D-galactoside (VII) and syrupy methyl 2,3,4,6-tetra-*O*-methyl-α-D-galactoside which was identified by conversion into the corresponding crystalline anilide.

A crystalline substance identical with the crystalline " methyl fluorogalactoside A " (III) was obtained by crystallization together of methyl α-glycosides of 6-*O*-methyl- and 6-deoxy-6-fluoro-galactose (XII and VI) in the proportion 2 : 1 by weight. It is clear therefore that the conjectured " methyl fluorogalactoside A " is an isomorphous mixture of those two compounds. This case and that of the close similarity in crystal structure[3] of (±)-2-deoxy-2-fluoroerythritol and erythritol itself suggest that isomorphous mixtures may be expected frequently among fluorinated polyhydric alcohols. Methylation of the

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* Part II, *J.*, 1960, 106.

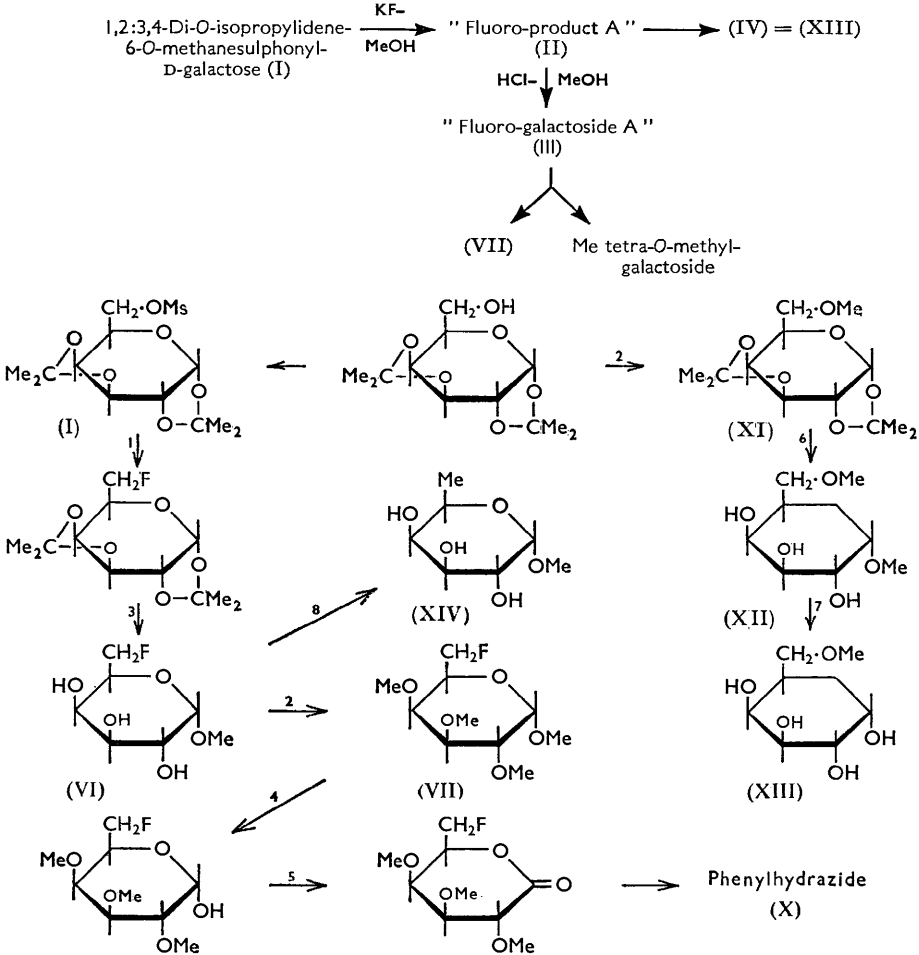
[1] Taylor and Kent, *J.*, 1958, 872.

[2] Munro and Percival, *J.*, 1936, 640; Freudenberg and Smeykal, *Ber.*, 1926, **59**, 100.

[3] Bekoe and Powell, *Proc. Roy. Soc.*, 1959, *A*, **250**, 301.

crystalline " methyl fluorogalactoside A " as obtained from the product (II) or by co-crystallization gave the same fully methylated derivatives.

The evidence thus indicates that, at elevated temperatures, exchange with potassium fluoride in methanol results in competition between fluoride and methoxide ions (formation of the latter ion probably being promoted by the alkalinity of the medium). It must be pointed out that Helferich and Gnüchtel[4] successfully employed these reagents without simultaneous methylation in the case of 3,5-*O*-benzylidene-1,2-isopropylidene-6-*O*-methanesulphonyl-D-glucose. There, however, the ester was more reactive[5] and exchange occurred at a lower temperature than with our galactose derivative. Replacement of sulphonyloxy esters by methoxy has already been noted.[6] Difficulty has been experienced in achieving



Reagents: 1, KF–$(CH_2{\cdot}OH)_2$. 2, MeI–Ag_2O. 3, HCl–MeOH. 4, H^+. 5, Br_2. 6, H^+–MeOH. 7, H^+–H_2O. 8, H_2–Ni.
Ms = $CH_3{\cdot}SO_2$.

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[4] Helferich and Gnüchtel, *Ber.*, 1941, **74**, 1035.

[5] Taylor, *Nature*, 1958, **182**, 660.

[6] Stoll, *Z. physiol. Chem.*, 1937, **207**, 147; 1937, **246**, 1; Helferich and Gnüchtel, *Ber.*, 1938, **71**, 712; Shoppee and Summers, *J.*, 1952, 1786, 1790.

paper-chromatographic separation of corresponding fluoro- and *O*-methyl-sugars: this can, however, be carried out by use of a water-saturated mixture of pyridine and butanol.[7]

Authentic methyl 6-deoxy-6-fluoro-α-D-galactoside (VI) was readily methylated without dehalogenation by methyl iodide and silver oxide, giving the corresponding 2,3,4-tri-*O*-methyl ether (VII) in high yield. The latter was readily hydrolysed by aqueous acid to the corresponding fluoro-tri-*O*-methyl-sugar (VIII) which with aqueous bromine gave 6-deoxy-6-fluoro-2,3,4-tri-*O*-methyl-D-galactono-1,5-lactone (IX). This compound was a syrup having a rate of hydrolysis (in aqueous media) similar to that of other 1,5-lactones [8] and was characterized by conversion into the crystalline phenylhydrazide (X). Bromine oxidation of the methylated fluoro-sugar was accompanied by little decomposition, in contrast to (±)-2-fluoro-3-hydroxypropanal which, under similar conditions, is extensively dehalogenated.[9]

It appears that methylation with silver oxide and methyl iodide provides a suitable means of investigations of ω-fluoro-hydroxy-compounds. Attempts to dehalogenate methyl 6-deoxy-6-fluoro-α-D-galactoside (VI) with Raney nickel and hydrogen at 1 atmosphere, with Raney nickel in boiling 70% aqueous ethanol, or with aluminium amalgam were unsuccessful, the starting material being recovered in every case.

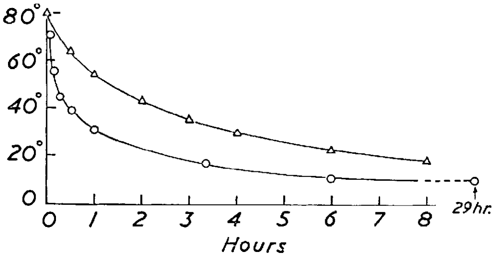

FIG. 1. *Mutarotation of 6-deoxy-6-fluoro-2,3,4-tri-O-methyl-D-galactono-1,5-lactone* (o) *and 2,3,4-tri-O-methyl-D-galactono-1,5-lactone* (Δ) (*c* 0·36 *in water*).

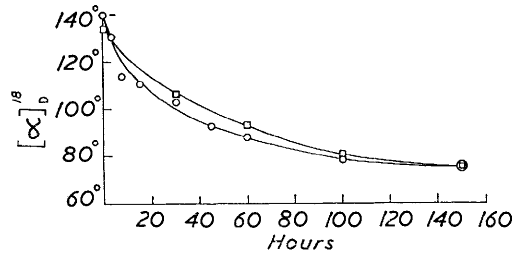

FIG. 2. *Mutarotation of 6-deoxy-6-fluoro-α-D-galactose* (○) *and α-D-galactose* (□) (*c* 0·4 *in water*).

Defluorination occurred, however, when methyl 6-deoxy-6-fluoro-α-D-galactoside (VI) was heated with Raney nickel in methanol at 100° with hydrogen at 120 atmospheres for 9 hr. Hydrolysis of the product (XIV) with aqueous acid yielded D-fucose, identified chromatographically and as the crystalline benzylphenylhydrazone.

Infrared spectral examination [10] of methyl 6-deoxy-6-fluoro-α-D-galactoside (VI) and its fully methylated derivative (VII) provided further evidence of the normal pyranosidic arrangement of these sugars. Absorption bands were found at 911, 963, 907, and 957 $cm.^{-1}$ characteristic of the galactopyranoside structure (Type 1 bands).[11] Type 2a absorption bands were present at 826 and 818 $cm.^{-1}$, and Type 2c (due to equitorial 4-H) at 865, 882, and 886. Breathing-frequency (Type 3) bands were present at 782 and 766 $cm.^{-1}$. In

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[7] Chargaff, Levine, and Green, *J. Biol. Chem.*, 1948, **175**, 67.

[8] Haworth, Ruell, and Westgarth, *J.*, 1924, **125**, 2468; Haworth, " The Constitution of Sugars," London, Arnold, 1929, p. 23.

[9] Kent, Hebblethwaite, and Taylor, *J.*, 1960, 106.

[10] Barker, Bourne, and Whiffin, " Methods of Biochemical Analysis," Vol. III, Interscience Publ., New York, 1956, p. 213.

[11] Challinor, Haworth, and Hirst, *J.*, 1931, 258.

addition, intense absorption was observed in the region 1000—1100 cm.$^{-1}$ consistent with the presence of fluorine.

The introduction of a fluorine atom at position 6 of galactose influences the reactivity at position 1. 6-Deoxy-6-fluoro-2,3,4-tri-*O*-methyl-D-galactono-1,5-lactone is hydrolysed (" mutarotates ") in neutral solution more rapidly (Fig. 1) than the usual 2,3,4-tri-*O*-methyl galactonolactone.[11] Both lactones have $[\alpha]_D$ of the same sign and order of magnitude and are clearly distinguished from 2,3,5-tri-*O*-methyl-D-galactono-1,4-lactone which mutarotates very much more slowly [12] {$[\alpha]_D$ $-37° \longrightarrow -32°$ (*c* 0·7 in H_2O) still incomplete after 5 days}. 6-Deoxy-6-fluoro-α-D-galactose mutarotates (Fig. 2) in aqueous solution at rate similar to that of the α-D-galactose, the rate constants ($\log_{10}$ at 20°) being $(1{\cdot}17 \pm 0{\cdot}1) \times 10^{-2}$ and $(1{\cdot}15 \pm 0{\cdot}1) \times 10^{-2}$ min.$^{-1}$ respectively. The results suggest that, in neutral conditions, the fluorine atom has little inductive effect on the ring-oxygen atom and on ring opening.[13]

In contrast, methyl 6-deoxy-6-fluoro-α-D-galactoside (VI) and its fully methylated derivative (VII) are more resistant to aqueous acids at 100° than is methyl α-D-galactoside. The rate of hydrolysis followed first-order kinetics in each case (see Table), as calculated from the usual equation, $-kt = \log_{10} [(\alpha_0 - \alpha)/(\alpha_t - \alpha)]$ where α_0, α_t, and α represent the values of optical rotatory power, initially, after *t* minutes, and finally.

Values of hydrolysis constants (10^2k, *min.*$^{-1}$) *of* 6-*fluorogalactose derivatives.*

Conc. of H_2SO_4 (M)	Me α-D-galactoside	Me 6-deoxy-6-fluoro-α-D-galactoside	Me 6-deoxy-6-fluoro-2,3,4-tri-*O*-methyl-α-D-galactoside
0·5	5·3 ± 0·3	2·9 ± 0·3	0·8 ± 0·1
1	12·7 ± 1·0	9·4 ± 0·6	3·5 ± 0·5

In these acid-catalysed reactions, the results suggest a protective action of the fluorine atom on the site of H_3O^+ attack. This may be explained on the basis of hydrogen-bonding between fluorine and H_3O^+ such that the resulting cationic centre, being equatorially disposed at position 6, restricts the approach of catalytic hydroxonium ion to the ring-oxygen atom.

EXPERIMENTAL

Paper Chromatography.—This was by downward elution on Whatman No. 1 with butan-1-ol–ethanol–water (4 : 1 : 5, v/v) or a water-saturated mixture of pyridine and butanol [7] (1 : 4, v/v). Reducing sugars were detected with aniline hydrogen phthalate.

Analyses.—Fluorine analyses were performed spectrometrically by Mr. F. T. Birks, A.E.R.E., Harwell, titrimetrically by Mr. L. F. Thomas, Porton, Wilts., and by Dr. A. Burchardt, Mülheim, Ruhr.

Action of Hydrated Potassium Fluoride on 1,2:3,4-*Di*-O-*isopropylidene*-6-O-*methanesulphonyl*-D-*galactose* (I) *in Anhydrous Methanol.*—The ester (I) (6 g.) was heated with potassium fluoride dihydrate (6 g.) in dry methanol (60 ml.) in a sealed tube at 150° for 18 hr. The potassium methanesulphonate which separated in almost quantitative yield was filtered from the cooled mixture and washed with methanol (5 ml.), and the combined filtrate and washings were concentrated under reduced pressure to about 10 ml. The products from three such experiments were combined, and water (100 ml.) was added. The filtered solution was extracted with ether (3 × 100 ml.), and the ether extract was dried ($MgSO_4$). Removal of the solvent afforded the product (designated fluoro-product A) (II) as a colourless syrup (6·26 g.), b. p. 96°/0·05 mm., n_D^{18} 1·4544 [Found: C, 55·2; H, 7·75; OMe, 8·2; F, 5·0%; *M* (Rast), 226. Calc. for $C_{12}H_{19}O_5F$: C, 54·9; H, 7·2; F, 7·2%; *M*, 262].

A product (1·85 g.) was also isolated having b. p. 100—110°/0·04 mm., n_D^{18} 1·4590 (Found: C, 69·9; H, 10·1; OMe, 9·1%). This was not investigated further.

Methanolysis of " Fluoro-product A " (II).—The product (II) (2·01 g.) was refluxed for 4 hr. with dry methanolic 1·4% (w/v) hydrogen chloride (60 ml.). The optical rotation changed from $[\alpha]_D^{16}$ $-19{\cdot}9° \longrightarrow -3{\cdot}1°$ (final value). The solution was then neutralized with lead

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[12] Luckett and Smith, *J.*, 1940, 1114.

[13] Swain and Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 2534.

carbonate, filtered, and evaporated under reduced pressure to about 5 ml. Ether was added and the product, designated " fluorogalactoside A " (III), obtained after 12 hr. was recrystallised from methanol–ether. It (0·4 g.) had m. p. 120°, $[\alpha]_D^{20}$ +161° (*c* 0·2 in H_2O) (Found: C, 44·8; H, 7·0; OMe, 22·4; F, 4·1. $C_8H_{16}O_6$ requires C, 46·15; H, 7·7; OMe, 29·8%). The compound consumed 2 mols. of periodate with the liberation of 1 mol. of formic acid.

Hydrolysis of " Fluoro-product A " (II) with Aqueous Acid.—The product (II) (1·587 g.) was heated in 0·05N-sulphuric acid (25 ml.) at 100° for 4·5 hr. {$[\alpha]_D$ −8·8° $\longrightarrow$ +51° (constant)}. The solution was neutralized with barium hydroxide, filtered and evaporated to dryness under reduced pressure. The sugar (0·8 g.) extracted from the residue with hot chloroform and recrystallized from methanol–ether had m. p. 122°, $[\alpha]_D^{20}$ +129° $\longrightarrow$ +53·5° (*c* 0·2 in H_2O) (Found: C, 43·1; H, 6·9; OMe, 15·1; F, 0. Calc. for $C_7H_{14}O_6$: C, 43·3; H, 7·2; OMe, 16·0%). The compound (IV) consumed 4 mols. of periodate and liberated 3 mols. of formic acid. Kuhn–Roth oxidation gave no indication of *C*-Me groups. When mixed with 6-*O*-methyl-α-D-galactopyranose no depression in m. p. was observed. Paper chromatography of the crystalline product (IV) in butanol–pyridine showed one constituent (R_F 0·31) identical with 6-*O*-methyl-D-galactose. The methanolic mother-liquor contained two substances, of R_F 0·31 and 0·37 (cf. R_F 0·37 for 6-deoxy-6-fluoro-D-galactose).

Methylation of " Fluorogalactoside A " (III).—The galactoside (III) (1·156 g.) was methylated three times with methyl iodide (10 ml.) and silver oxide (2 g.). The product (1 g.) partially crystallized. After recrystallization from ether, the first component (0·8 g.) had m. p. 109—110° alone or mixed with methyl 6-deoxy-6-fluoro-2,3,4-tri-*O*-methyl-α-D-galactoside (VII) and $[\alpha]_D$ +150° (*c* 0·5 in $CHCl_3$) (Found: C, 50·2; H, 7·3; F, 9·2; OMe, 50·9. Calc. for $C_{10}H_{19}O_5F$: C, 50·4; H, 8·0; F, 7·6; OMe, 50·0%). The non-crystalline material, after distillation [0·35 g.; b. p. 104—105°/0·04 mm. (bath-temp.), n_D^{20} 1·4420; OMe, 60·1%] was hydrolysed with N-sulphuric acid (8 ml.) for 5 hr. at 100°. The solution was neutralized with barium carbonate, filtered, and evaporated to a reducing syrup (0·21 g.; n_D^{20} 1·4540; OMe, 48·2%). The last sugar (0·17 g.) was refluxed with aniline (85 mg.) in ethanol (8·5 g.) for 10 hr. Removal of the solvent in the presence of 1 ml. of added benzene yielded a syrup which crystallized readily from acetone–light petroleum and then had m. p. 189—190° alone or mixed with 2,3,4,6-tetra-*O*-methyl-D-galactosylaniline.

Methyl 6-O-*Methyl-α-D-galactoside* (XIII).—Di-*O*-isopropylidene-D-galactose (5 g.) was methylated three times with methyl iodide and silver oxide in the usual manner. The resulting 6-*O*-methyl derivative (XI) (4 g.; n_D^{21} 1·4546, b. p. 92°/0·02 mm.) was refluxed with 1% (w/v) methanolic hydrogen chloride (25 ml.) for 5 hr. The solution was neutralized with silver carbonate and concentrated under reduced pressure. The resulting *methyl* 6-O-*methyl-α-D-galactoside* (XII), recrystallized from ether–methanol, had m. p. 132—133°, $[\alpha]_D^{20}$ +171° (*c* 4·3 in H_2O) (Found: C, 46·0; H, 7·6; OMe, 30·0. $C_8H_{16}O_6$ requires C, 46·15; H, 7·7; OMe, 29·8%). The galactoside consumed two mols. of sodium metaperiodate, liberating 1 mol. of formic acid. Hydrolysis of the glycoside (XII) gave 6-*O*-methyl-α-D-galactose [2] which, crystallized from dry methanol, had m. p. 122° and $[\alpha]_D^{20}$ +66° (equil.) (*c* 0·5 in H_2O) (Found: OMe, 15·9. Calc. for $C_7H_{14}O_6$: OMe, 15·98%), R_F 0·46 in butanol–ethanol–water, 0·31 in butanol–pyridine.

Formation of " Fluoro-galactoside A " by Co-crystallization.—Authentic methyl 6-deoxy-6-fluoro-α-D-galactoside (VI) (0·2 g.), mixed with methyl 6-*O*-methyl-α-D-galactoside (XII) (0·4 g.), was recrystallized three times from methanol–ether. The product had m. p. 120° alone or mixed with " fluoro-galactoside A " (III) and $[\alpha]_D^{19}$ +158° (*c* 0·8 in H_2O) (Found: C, 44·6; H, 6·9; OMe, 21·8; F, 4·0%).

*Methyl 6-Fluoro-2,3,4-tri-*O*-α-D-galactoside* (VII).—Methyl 6-deoxy-6-fluoro-α-D-galactoside (VI) (0·45 g.), prepared by Taylor and Kent's method,[1] was refluxed three times with methyl iodide (15 ml.), dry acetone (2 ml.), and dry silver oxide (2 g.) for 19 hr., each time. Fresh silver oxide (0·5 g.) was added after 2 hr. in each case. Filtration and concentration of the final solution gave a syrup from which *methyl 6-deoxy-6-fluoro-2,3,4-tri-*O*-methyl-α-D-galactoside* (VII) crystallized as large prisms. After recrystallization from acetone the product (0·35 g.) had m. p. 110°, $[\alpha]_D^{20}$ +151° (*c* 0·6 in $CHCl_3$) (Found: C, 50·1; H, 7·9; F, 7·5; OMe, 52·4. $C_{10}H_{19}O_5F$ requires C, 50·4; H, 8·0; F, 8·0; OMe, 52·0%).

*6-Deoxy-6-fluoro-2,3,4-tri-*O*-methyl-α-D-galactose* (VIII).—The fully methylated galactoside (VII) (0·75 g.) was heated at 100° with N-sulphuric acid (100 ml.) for 8 hr. The following change in $[\alpha]_D$ was observed: +171° ± 2° (0 hr.), +125° ± 2° (4 hr.), +107° ± 2° (7 hr.), +103° ± 2° (constant) (8 hr.). The solution was brought to near-neutrality with barium hydroxide and finally neutralized with barium carbonate. The filtrate was evaporated to dryness under reduced pressure and the 6-*deoxy*-6-*fluoro*-2,3,4-*tri*-O-*methyl*-D-*galactose* (VIII) was obtained by extracting the residue repeatedly with chloroform. The fully methylated sugar was obtained as a colourless syrup (0·6 g.), R_F 0·69 in butanol–ethanol–water, n_D^{23} 1·4560 (Found: C, 47·7; H, 7·45; F, 7·6; OMe, 40·8. $C_9H_{17}O_5F$ requires C, 48·2; H, 7·6; F, 8·1; OMe, 41·5%). This sugar and its anilide have so far resisted crystallization.

6-*Deoxy*-6-*fluoro*-2,3,4-*tri*-O-*methyl*-D-*galactono*-1,5-*lactone* (IX).—This trimethyl sugar (VIII) (0·44 g.) was dissolved in water (5 ml.) containing bromine (1 ml.). At intervals, samples were removed, freed from bromine by aeration, and tested with Fehling's solution. When, after 10 days, the solution no longer had reducing properties, excess of bromine was removed and the solution filtered. The filtrate, neutralized with silver carbonate, was saturated with hydrogen sulphide and again filtered. Removal of the solvent under reduced pressure gave a pale yellow mobile syrup considered to be 6-deoxy-6-fluoro-2,3,4-tri-*O*-methyl-D-galactonic acid. This was lactonized when heated at 100°/15 mm. for 3 hr. The lactone was taken up in ether and filtered to remove traces of silver sulphide. Concentration of the ethereal solution gave 6-*deoxy*-6-*fluoro*-2,3,4-*tri*-O-*methyl*-D-*galactono*-1,5-*lactone* (0·16 g.), b. p. 50—55°/0·05 mm., n_D^{20} 1·4520 (Found: C, 48·2; H, 6·2; OMe, 41·6. $C_9H_{15}O_5F$ requires C, 48·7; H, 6·8; OMe, 41·9%), $[\alpha]_D^{22}$ $+71°$ (3 min.) $\longrightarrow$ $+11°$ (6 hr., equil.) (*c* 0·36 in H_2O), giving initially a positive hydroxamic acid test.

6-*Deoxy*-6-*fluoro*-2,3,4-*tri*-O-*methyl*-D-*galactose Phenylhydrazide* (X).—The trimethyl-lactone (IX) (50 mg.) was heated with phenylhydrazine (40 ml.) in dry ethanol (5 ml.) for 1½ hr. The solvent was removed and the residue was heated at 100° for a further 30 min. The remaining syrup crystallized on addition of ligroin (b. p. 40—60°), and the *phenylhydrazide* recrystallized from ethanol (yield 15 mg.; m. p. 151—152°) (Found: C, 54·0; H, 6·8; N, 8·1. $C_{15}H_{23}O_5N_2F$ requires C, 54·8; H, 7·0; N, 8·7%).

6-*Deoxy*-6-*fluoro*-D-*galactose Phenylosazone*.—The fluoro-sugar [1] (0·1 g.) was heated in water (0·5 ml.) at 100° for 1 hr. with a solution (2 ml.) of phenylhydrazine (2 g.) and glacial acetic acid (1·5 ml.) in water (15 ml.). The *phenylosazone* (50 mg.) had m. p. 155—156° (from benzene) (Found: C, 59·2; H, 5·6; N, 13·5; F, 4·9. $C_{18}H_{21}O_3N_4F$ requires C, 60·0; H, 5·8; N, 15·6; F, 5·2%).

Hydrogenation of Methyl 6-*Deoxy*-6-*fluoro*-α-D-*galactoside* (VI).—The fluoro-galactoside (0·5 g.) and pyrophoric Raney nickel (1 g.) in methanol (50 ml.) were treated with hydrogen at 100°/120 atm. for 9 hr. The filtered solution was evaporated and the residue extracted with chloroform (3 × 50 ml.). After removal of the solvent, the reduced product (XIV) was hydrolysed with 0·5N-sulphuric acid (5 ml.) at 100° for 2 hr. The resulting reducing sugar (R_F 0·39 in butanol–ethanol–water) was converted into the benzylphenylhydrazone, which after recrystallization from ethanol had m. p. 177—178° alone or mixed with D-fucose benzylphenylhydrazone.

Rates of Hydrolysis.—These were measured polarimetrically for solutions (10 ml.) in the appropriate concentration of sulphuric acid (0·5M or 1·0M). The solutions were heated at 100°, then cooled rapidly to 25° before the measurement of optical rotations. Methyl 6-deoxy-6-fluoro-α-D-galactopyranoside (50 mg.), methyl 6-deoxy-6-fluoro-α-D-galactoside (50 mg.), and methyl 6-deoxy-6-fluoro-2,3,4-tri-*O*-methyl-α-D-galactoside (50 mg.) were studied.

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