249. 2,3,4,6-*Tetra-O-benzyl-*D*-galactosyl Chloride and its Use in the Synthesis of* α- *and* β-D-*Galactopyranosides.*

By P. W. Austin, F. E. Hardy, J. G. Buchanan, and J. Baddiley.

2,3,4,6-Tetra-*O*-benzyl-α-D-galactose has been synthesised and converted, by treatment with thionyl chloride, into the corresponding galactosyl chloride which has been shown to be mainly the α-anomer. Conditions are described for the use of the chloride in the synthesis of α- and β-D-galactosides, and syntheses of the α- and β-anomers of 2-*O*-D-galactosylglycerol and 2-*O*-D-galactosyl-D-erythritol are reported.

The recent synthesis of 2,3,4,6-tetra-*O*-benzyl-D-glucosyl chloride has provided a simple general method for the preparation of α-D-glucosides.[1] Treatment of the chloride with an alcohol in the presence of silver perchlorate and silver carbonate gives a mixture of the corresponding α- and β-glucosides containing a high proportion of the α-anomer; the mixture is readily resolved by chromatography on Dowex-1 resin in the hydroxide form.[2]

α-D-Galactopyranosides, like the corresponding glucosides, are difficult to prepare and several attempts have been made to find a general synthetical route to these compounds: (1) modification of the Koenigs–Knorr reaction for the synthesis of β-galactosides by replacing the silver salt catalyst with either quinoline [3] or mercuric bromide–mercuric cyanide; [4] (2) anomerisation of the acetate of a β-galactoside; [5] (3) reaction of 1-*O*-(2′,4′,6′-trimethylbenzoyl)-β-D-galactose with alcohols in the presence of an acid catalyst.[6] In the present work another approach to this problem has been examined; this involves synthesis of 2,3,4,6-tetra-*O*-benzyl-D-galactosyl chloride (III) and treatment of this derivative with alcohols under similar conditions to those used in the synthesis of α-glucosides from the corresponding glucosyl chloride.

Benzylation of methyl β-D-galactopyranoside with benzyl chloride–potassium hydroxide gave the crystalline tetra-*O*-benzyl derivative (I) which was converted by treatment with dilute acid into crystalline 2,3,4,6-tetra-*O*-benzyl-D-galactose (II); observation of the mutarotation of this sugar in pyridine–phenol suggests that it possesses the α-configuration. It could also be prepared similarly from methyl α-D-galactopyranoside but the acid hydrolysis in this case was more difficult. Treatment of the sugar (II) with thionyl chloride under carefully controlled conditions gave the galactosyl chloride (III); the specific rotation of this material suggests that it is mainly the α-anomer and indeed treatment with sodium methoxide followed by catalytic hydrogenolysis of the product gave a mixture of methyl α- and β-D-galactosides containing over 90% of the β-anomer.

In order to examine the nature of the glycosidic linkages formed when this galactosyl chloride reacts with alcohols in the presence of silver perchlorate–silver carbonate, two galactosides, 2-*O*-D-galactosylglycerol and 2-*O*-D-galactosyl-D-erythritol, were synthesised from the halide. These particular syntheses were devised since the products could be used to confirm structures assigned to two galactosides on the basis of analytical data. Floridoside, a galactoside occurring in many red algae, was shown by Putman and Hassid [7] to be 2-*O*-α-D-galactosylglycerol (IV) and although this compound was later prepared by degradation of 3-*O*-α-D-galactosyl-L-arabinose [8] it was thought that a synthesis from glycerol and galactose would be of interest. A galactoside which appeared to be either 2-*O*-α- or 2-*O*-β-D-galactosyl-D-erythritol was recently isolated in these laboratories by

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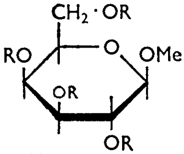
[1] P. W. Austin, F. E. Hardy, J. G. Buchanan, and J. Baddiley, *J.*, 1964, 2128.
[2] P. W. Austin, F. E. Hardy, J. G. Buchanan, and J. Baddiley, *J.*, 1963, 5350.
[3] B. Helferich and H. Bredereck, *Annalen*, 1928, **465**, 173.
[4] B. Helferich and J. Zirner, *Chem. Ber.*, 1962, **95**, 2604.
[5] B. Wickberg, *Acta Chem. Scand.*, 1958, **12**, 1187.
[6] B. Helferich and D. V. Kashelikar, *Chem. Ber.*, 1957, **90**, 2094.
[7] E. W. Putman and W. Z. Hassid, *J. Amer. Chem. Soc.*, 1954, **76**, 2221.
[8] A. J. Charlson, P. A. J. Gorin, and A. S. Perlin, *Canad. J. Chem.*, 1956, **34**, 1811; 1957, **35**, 365.

degradation of the *Pneumococcus* type 11A specific substance according to the method of Smith and his collaborators[9] (Dr. D. A. Kennedy, unpublished) and thus a synthesis of both anomers was desirable.

In the presence of silver perchlorate and silver carbonate 2,3,4,6-tetra-*O*-benzyl-D-galactosyl chloride (III) reacted smoothly with 1,3-di-*O*-benzylglycerol and paper chromatography of the product after purification and hydrogenolysis revealed the presence of 2-*O*-galactosylglycerol and a component which was probably 1-*O*-galactosyl galactoside. Chromatography of the mixture on Dowex-1 resin in the hydroxide form gave crystalline 2-*O*-α-D-galactosylglycerol (IV) in good yield; this material was shown by comparison of m. p.s and infrared spectra to be identical with floridoside. An attempt was made to prepare this α-galactoside by treating 1,3-di-*O*-benzylglycerol with 2,3,4,6-tetra-*O*-acetyl-α-D-galactosyl bromide in the presence of mercuric bromide and mercuric cyanide, an approach which has been used recently in a synthesis of 2-*O*-α-D-galactosyl-α-D-glucose.[4] However, under these conditions 2-*O*-β-D-galactosylglycerol (V) was the only isolable product.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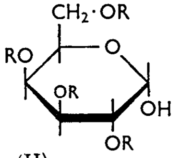
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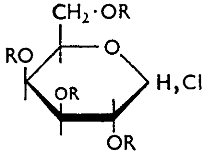
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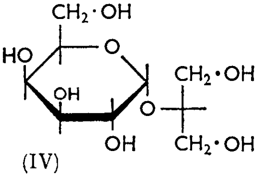
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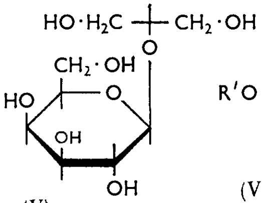
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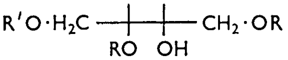
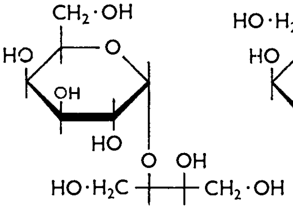

$R'O{\cdot}H_2C-\underset{RO}{C}-\underset{OH}{C}-CH_2{\cdot}OR$

(VI: R′ = H)

(VII: R′ = CO·$C_6H_4{\cdot}NO_2$-*p*)

[R = $CH_2{\cdot}Ph$]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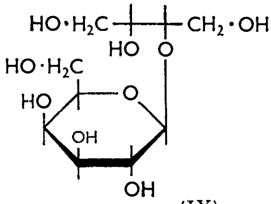
(IX)

For the synthesis of 2-*O*-D-galactosyl-D-erythritol a derivative of erythritol was prepared with only the 2-hydroxyl (D-form) free. Benzylation of 2,4-*O*-benzylidene-D-erythritol[10] with benzyl chloride–potassium hydroxide followed by mild acid hydrolysis gave 1,3-di-*O*-benzyl-D-erythritol (VI) which was converted into its crystalline 4-*O*-*p*-nitrobenzoyl derivative (VII). This material was treated with 2·8 mol. of the galactosyl chloride (III) in the usual way and the product, after deacylation with methanolic ammonia, was chomatographed on alumina. Two of the fractions were subjected to catalytic hydrogenolysis with palladium and the products were identified as 1-*O*-D-galactosyl galactoside and 2-*O*-D-galactosyl-D-erythritol. The nonreducing disaccharide of galactose was further separated into the αα- and αβ-anomers by chromatography on Dowex-1 resin in the hydroxide form. The αβ-anomer was identical with material prepared recently by Helferich and Zirner[4] but the m. p. and specific rotation differed markedly from those reported by earlier workers.[11,12] Unexpectedly, the α- and β-anomers of 2-*O*-D-galactosyl-D-erythritol could not be separated by chromatography on Dowex-1 resin. However, fractional crystallisation of the mixture and of its acetate did give the pure α- and β-anomers

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[9] M. Abdel-Akher, J. K. Hamilton, R. Montgomery, and F. Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 4970; I. J. Goldstein, G. W. Hay, B. A. Lewis, and F. Smith, Amer. Chem. Soc. Meeting, Boston, April 1959, Abs. Papers, 3D.

[10] D. L. MacDonald, H. O. L. Fischer, and C. E. Ballou, *J. Amer. Chem. Soc.*, 1956, **78**, 3720.

[11] H. Vogel and H. Debowska-Kurnicka, *Helv. Chim. Acta*, 1928, **11**, 910.

[12] V. E. Sharp and M. Stacey, *J.*, 1951, 285.

(VIII, IX) (25·5 and 7·7% yield from the *p*-nitrobenzoate, respectively). The β-anomer was shown by comparison of m. p.s and infrared spectra to be identical with the degradation product of the capsular material from *Pneumococcus* type 11A.

Since other methods for synthesising α-D-galactosides either can be applied only in certain cases or give products in very low yield, the reaction of 2,3,4,6-tetra-*O*-benzyl-D-galactosyl chloride with alcohols under the specified conditions provides the first generally applicable method for the synthesis of α-D-galactosides in good yield.

EXPERIMENTAL

Infrared spectra were determined on potassium bromide discs. Chromatographic separations were carried out on either silica gel (Hopkin and Williams), alumina (Savory and Moore), or Dowex-1 resin (2% cross-linkages; 200—400 mesh; OH^- form).

Paper Chromatography.—Whatman No. 4 paper was used with the solvent system butan-1-ol–ethanol–water–ammonia (*d*, 0·88) (40 : 10 : 49 : 1) [13] descending. The periodate–Schiff [14] and silver nitrate–sodium hydoxide [15] reagents were used as sprays where appropriate.

2,3,4,6-*Tetra-*O*-benzyl-α-*D-*galactose.*—(*a*) A mixture of methyl β-D-galactopyranoside (14·3 g.), benzyl chloride (100 ml.), powdered potassium hydroxide (50 g.), and dioxan (150 ml.) was stirred at 100° for 2 hr. Benzyl chloride (50 ml.) and powdered potassium hydroxide (50 g.) were added and the stirring at 100° was continued for a further 18 hr. The mixture was diluted with dioxan (100 ml.) and filtered through " Hyflo " silica. The filtrate and washings were evaporated to a syrup at 140°/2 mm.; this material crystallised on trituration with cyclohexane–light petroleum (b. p. 60—80°). Recrystallisation from light petroleum (b. p. 60—80°) gave *methyl* 2,3,4,6-*tetra-*O*-benzyl-β-*D-*galactoside* as needles (27·4 g., 67%), m. p. 80—81°, $[\alpha]_D$ +18° (*c* 3·6 in dioxan) (Found: C, 76·1; H, 6·8; OMe, 5·9. $C_{35}H_{38}O_6$ requires C, 75·8; H, 6·9; OMe, 5·6%).

A solution of this galactoside (19·4 g.) in a mixture of dioxan (280 ml.), water (72 ml.), and 10N-sulphuric acid (7·8 ml.) was heated under reflux for 8 days. On cooling, the solution was neutralised ($CaCO_3$), filtered through " Hyflo " silica, and evaporated to a syrup. This material was dissolved in a little benzene and chromatographed on alumina (200 g.); elution with benzene–ether (9 : 1; 500 ml.) gave unchanged galactoside (2·7 g.) while elution with ether–ethanol (9 : 1; 400 ml.) gave a syrup which crystallised from cyclohexane. Recystallisation from ether–light petroleum (b. p. 40—60°) gave 2,3,4,6-*tetra-*O*-benzyl-α-*D-*galactose* (10·7 g.), m. p. 66—68°, $[\alpha]_D$ +82·5° (5 min.) $\longrightarrow$ +74° (final) [*c* 1·0 in pyridine–phenol (9 : 1)] (Found: C, 75·5; H, 6·6. $C_{34}H_{36}O_6$ requires C, 75·5; H, 6·7%).

(*b*) Benzylation of methyl α-D-galactopyranoside hydrate (39·5 g.) with benzyl chloride–potassium hydroxide under conditions similar to those described above gave crude *methyl* 2,3,4,6-*tetra-*O*-benzyl-α-*D-*galactoside* as a syrup (99 g.) (Found: C, 75·1; H, 6·8; OMe, 6·5%). Treatment of this material with sulphuric acid followed by chromatography of the product on alumina as described above gave unhydrolysed glycoside (47·8 g.) and 2,3,4,6-*tetra-*O*-benzyl-α-*D-*galactose* (35·8 g.), m. p. 66—68°, $[\alpha]_D$ +77° (*c* 2·3 in benzene). A further quantity of this sugar (22·6 g.) was obtained from the unhydrolysed material by means of a second acid hydrolysis.

1-O-*Acetyl-*2,3,4,6-*tetra-*O*-benzyl-*D-*galactose.*—The above benzyl ether (10 g.) was acetylated with acetic anhydride in pyridine and the acetate was isolated by use of chloroform as a syrup (10·6 g.), $[\alpha]_D$ +57° (*c* 5·0 in benzene), which partially crystallised on trituration with benzene. The crystals were washed with benzene and recrystallised from ethyl acetate–light petroleum (b. p. 60—80°) to give the β-*anomer* (3·5 g.), m. p. 99—101°, $[\alpha]_D$ +24° (*c* 2·9 in benzene) (Found: C, 73·9; H, 6·7. $C_{36}H_{38}O_7$ requires C, 74·3; H, 6·6%). The benzene washings were evaporated to dryness and the residue was recrystallised from ether–light petroleum (b. p. 40—60°) to give the α-*anomer* (3·1 g.), m. p. 67—69°, $[\alpha]_D$ +95° (*c* 2·0 in benzene) (Found: C, 74·6; H, 6·7%).

2,3,4,6-*Tetra-*O*-benzyl-*D-*galactosyl Chloride.*—2,3,4,6-Tetra-*O*-benzyl-α-D-galactose (5·17 g.) was dissolved in pure thionyl chloride (50 ml.) at 0° and the solution was maintained at this temperature for 2 days. After a further 2 days at room temperature, the solution was boiled for 30 min., diluted with toluene (100 ml.), and evaporated to dryness. The *galactosyl chloride,*

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[13] E. L. Hirst, L. Hough, and J. K. N. Jones, *J.*, 1949, 928.

[14] J. Baddiley, J. G. Buchanan, R. E. Handschumacher, and J. F. Prescott, *J.*, 1956, 2818; F. E. Hardy and J. G. Buchanan, *J.*, 1963, 5881.

[15] W. E. Trevelyan, D. P. Procter, and J. S. Harrison, *Nature*, 1950, **166**, 444.

freed from traces of thionyl chloride by evaporation with toluene (2 × 100 ml.), was a yellow syrup (5·2 g.), $[\alpha]_D$ +147° (*c* 2·0 in benzene) (Found: Cl, 6·4. $C_{34}H_{35}ClO_5$ requires Cl, 6·35%).

Reaction of 2,3,4,6-*Tetra*-O-*benzyl*-D-*galactosyl Chloride with Sodium Methoxide.*—A sample of the chloride (1·2 g.) was dissolved in methanol (100 ml.) containing sodium methoxide (from 0·2 g. of sodium). After 2 days at room temperature the solution was neutralised (solid carbon dioxide) and evaporated to dryness. The residue was extracted with benzene (70 ml.) and the extract was washed with water, dried (Na_2SO_4), and evaporated to a syrup (1·1 g.). This was dissolved in a little benzene and chromatographed on alumina (50 g.); elution with benzene–ether (9 : 1) gave material (1·0 g.) which was hydrogenated in ethanol (50 ml.) during 20 hr. by using palladium (from 1·0 g. of oxide). After filtration the solution was evaporated to a syrup (0·35 g.), $[\alpha]_D$ +32° (*c* 3·4 in water). Examination on paper showed that this material contained both methyl β- and α-D-galactopyranoside (R_{Glucose} 1·9 and 2·12). Crystallisation from ethanol gave the β-anomer (0·22 g., 53%), m. p. 172°. The mother-liquors were evaporated to dryness and the residue, in a little water, was chromatographed on a column (16 cm. × 1·7 cm.) of Dowex-1 (OH^-) resin; material was eluted with water and the eluate was collected in fractions (10 ml.).[2] Fractions 6 and 7 contained the α-anomer (0·025 g., 6%), m. p. 105°, while fractions 8—11 contained more of the β-anomer (0·05 g., 12%).

2-O-α-D-*Galactopyranosylglycerol.*—1,3-Di-*O*-benzylglycerol [1] (0·26 g.), silver carbonate (2·25 g.), and Drierite (7·5 g., regular grade) were added to pure, dry benzene (40 ml.). Silver perchlorate (0·25 g.) was dissolved in benzene (80 ml.), and solvent (30 ml.) was removed by distillation; this solution was then added to the mixture which was stirred overnight in the dark. A solution of the galactosyl chloride (1·1 g., 2·1 mol.) in benzene (33 ml.) was introduced during 4 hr. with stirring in the dark. After the mixture had been stirred for a further 66 hr. it was filtered through " Hyflo " silica and the filtrate was washed with water, dried (Na_2SO_4), and evaporated to a syrup (1·17 g.). This material, dissolved in a little benzene, was chromatographed on alumina (75 g.); elution with benzene–ether (1 : 1) gave a syrup (0·88 g.) which was hydrogenated in ethanol (40 ml.) during 20 hr. by using palladium (from 0·7 g. of oxide). After filtration the solution was evaporated to a syrup (0·34 g.); examination on paper showed the presence of two components ($R_{\text{Galactose}}$ 0·38 and 1·14) the faster of which had the same mobility as authentic 2-*O*-α-D-galactosylglycerol. This mixture was resolved by applying its aqueous solution to a column (31 cm. × 1·7 cm.) of Dowex-1 (OH^-) resin and then eluting with water. The progress of the separation was followed by observing the changes in the optical rotation of the eluate; a resolution into two dextrorotatory fractions was obtained. The first of these contained 2-*O*-α-D-galactosylglycerol; two recrystallisations from ethanol gave material (0·065 g., 27%), m. p. 129—130°, $[\alpha]_D$ +163° (*c* 1·0 in water) (Found: C, 42·6; H, 7·0. Calc. for $C_9H_{18}O_8$: C, 42·5; H, 7·15%). The m. p. of this compound was not depressed on mixing it with floridoside, and the infrared spectra of the two compounds were identical. Acetylation of impure 2-*O*-α-D-galactosylglycerol recovered from the ethanolic mother-liquors gave the hexa-*O*-acetyl derivative (0·15 g.), m. p. 101—102°, $[\alpha]_D$ +113° (*c* 0·9 in acetone), from ethanol (Found: C, 49·8; H, 5·8. Calc. for $C_{21}H_{30}O_{14}$: C, 49·8; H, 6·0%); Putman and Hassid [7] give m. p. 101°, $[\alpha]_D$ +114°, for this compound. The syrupy material from the second dextrorotatory fraction was shown, by examination on paper, to contain a futher amount of 2-*O*-D-galactosylglycerol (probably the β-anomer) as well as the component with $R_{\text{Galactose}}$ 0·38.

2-O-β-D-*Galactopyranosylglycerol.*—2,3,4,6-Tetra-*O*-acetyl-α-D-galactosyl bromide (4·15 g., 1 mol.) was added to anhydrous acetonitrile (28 ml.) containing 1,3-di-*O*-benzylglycerol (2·77 g.), mercuric cyanide (1·27 g.), and mercuric bromide (1·8 g.). After 17 hr. at room temperature, the solution was evaporated to dryness and the residue was extracted with methylene chloride (2 × 25 ml.). The methylene chloride solution was filtered through " Hyflo " silica, washed with 10% potassium bromide solution (4 × 50 ml.), dried (Na_2SO_4), and evaporated to a syrup (5·76 g.). This material was deacetylated catalytically with sodium methoxide in methanol. After neutralisation (solid carbon dioxide) the methanolic solution was evaporated to dryness and the residue was extracted with acetone (2 × 60 ml.). The acetone solution was filtered and evaporated to a syrup (3·77 g.). This material was added to liquid ammonia (100 ml.), and small pieces of sodium were added to the suspension until a permanent blue colour was observed. The residue obtained on evaporation of the ammonia was dissolved in ethanol (100 ml.), and this solution was neutralised (solid carbon dioxide), filtered through " Hyflo " silica, and evaporated to a syrup (2·0 g.). An aqueous solution of this material was de-ionised by use of Dowex-50 (H^+) and Dowex-1 (CO_3^{2-}) resins and then evaporated to dryness to give

2-*O*-β-D-galactosylglycerol which crystallised from ethanol as needles (0·33 g.), m. p. 134—135°, $[\alpha]_D$ −2·5° (*c* 2 in water) (Found: C, 42·6; H, 7·55. Calc. for $C_9H_{18}O_8$: C, 42·5; H, 7·15%); Charlson *et al.*[8] give m. p. 126—127°, $[\alpha]_D$ −2°.

1,3-*Di*-O-*benzyl*-4-O-p-*nitrobenzoyl*-D-*erythritol.*—2,4-*O*-Benzylidene-D-erythritol[10] (5·04 g.), powdered potassium hydroxide (50 g.), and benzyl chloride (20 ml.) were added to dioxan (110 ml.); the mixture was heated under reflux with vigorous mechanical stirring during 18 hr. and then filtered through " Hyflo " silica. The filtrate was evaporated to a syrup which was dissolved in a little light petroleum (b. p. 60—80°) and chromatographed on alumina (320 g.). Light petroleum (b. p. 60—80°) eluted dibenzyl ether while benzene–ether (19 : 1) eluted material which was then heated under reflux for 4·5 hr. with ethanol (140 ml.), water (20 ml.), and 10N-sulphuric acid (2 ml.). The solution was neutralised ($CaCO_3$), filtered through " Hyflo " silica, and evaporated to dryness. The residue was freed from benzaldehyde by steam-distillation and then dissolved in chloroform (200 ml.). The chloroform solution was washed with 0·1N-sodium hydroxide solution and water, dried (Na_2SO_4), and evaporated to a syrup. This material and *p*-nitrobenzoyl chloride (3·47 g.) were added to methylene chloride (20 ml.), and the solution was cooled to 0°. Ice-cold, anhydrous pyridine was added and the solution was kept at 0° overnight and then at room temperature for 3 days. The p-*nitrobenzoate* was isolated by use of chloroform and purified by chromatography on silica (330 g.); benzene–ether (19 : 1) eluted unidentified material while benzene–ether (4 : 1) eluted the required derivative (6·2 g., 58%) which, after two recrystallisations from ether–light petroleum (b. p. 40—60°), had m. p. 50°, $[\alpha]_D$ −2° (*c* 3·4 in dioxan) (Found: C, 66·5; H, 5·8; N, 3·5. $C_{25}H_{25}NO_7$ requires C, 66·5; H, 5·6; N, 3·1%).

Reaction between 1,3-*Di*-O-*benzyl*-4-O-p-*nitrobenzoyl*-D-*erthritol and* 2,3,4,6-*Tetra*-O-*benzyl*-D-*galactosyl Chloride.*—The above *p*-nitrobenzoate (1·52 g.), Drierite (20 g.), and silver carbonate (8 g.) were added to pure, dry benzene (100 ml.). Silver perchlorate (1·2 g.) was dissolved in benzene (100 ml.) and solvent (40 ml.) was removed by distillation; this solution was then added to the mixture which was stirred for 12 hr. in the dark. A solution of the galactosyl chloride (2·58 g., 1·4 mol.) in benzene (50 ml.) was added during 8 hr. with stirring in the dark. Stirring was continued for a further 16 hr. and then more of the galactosyl chloride (2·58 g.) in benzene (50 ml.) was added during 8 hr. After stirring in the dark for a further 6 days the mixture was filtered through " Hyflo " silica and the filtrate was washed with water, dried (Na_2SO_4) and evaporated to a syrup. This was dissolved in anhydrous methanol (400 ml.) previously saturated at 0° with dry ammonia and the solution was kept at room temperature overnight. Ammonia solution (10 ml.; *d* 0·88) was added and the solution was kept at room temperature for a further 24 hr. and evaporated to dryness. The residue was extracted with benzene (2 × 250 ml.); this extract was clarified by filtration and concentrated to a syrup (5·8 g.). This material was dissolved in a little benzene and chromatographed on alumina (200 g.); elution with benzene–ether–ethanol (80 : 19 : 1) gave a syrup (2·08 g.)—product 1, and elution with benzene–ether–ethanol (80 : 18 : 2) gave a second syrup (3·05 g.)—product 2. These two products were hydrogenated separately and the galactosides were isolated and identified as described below.

(*a*) *Product* 1. This was hydrogenated during 24 hr. by using palladium (from 1·1 g. of oxide) in ethanol (100 ml.). Filtration and evaporation to dryness gave a syrup (0·6 g.), $[\alpha]_D$ +160° (*c*, 2·0 in H_2O); chromatography on paper showed the presence of a major component with $R_{\text{Galactose}}$ 0·48. This material was dissolved in a little water and applied to a column (47 cm. × 2·1 cm.) of Dowex-1 (OH^-) resin; elution was with water at a flow-rate of 60 ml./hr., the eluate being collected in fractions (15 ml.). Fractions 18—27 contained 1-*O*-α-D-galactosyl-α-D-galactoside (0·29 g.), $[\alpha]_D$ +217° (*c* 2·0 in water). It was converted into its crystalline octa-acetate, m. p. 229°, $[\alpha]_D$ +179° (*c* 1·2 in chloroform) (Found: C, 49·3; H, 5·7. Calc. for $C_{28}H_{38}O_{19}$: C, 49·6; H, 5·65%); Bredereck *et al.*[16] give m. p. 227—228°, $[\alpha]_D$ +185°, for this compound. Fractions 30—42 contained 1-*O*-α-D-galactosyl β-D-galactoside (0·18 g.), $[\alpha]_D$ +120° (*c* 2·0 in water). Acetylation gave the crystalline octa-acetate, m. p. 148—149°, $[\alpha]_D$ +93° (*c* 1·4 in chloroform); the m. p. of this derivative was not depressed on mixing it with authentic material, m. p. 149—150°, $[\alpha]_D$ +97°, kindly provided by Professor B. Helferich.

(*b*) *Product* 2. This was hydrogenated in ethanol (200 ml.) during 24 hr. by using palladium (from 2·5 g. of oxide). Filtration and evaporation to dryness gave material (1·06 g.); examination on paper showed the presence of one component with $R_{\text{Galactose}}$ 0·87. The syrup, in a little

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[16] H. Bredereck, G. Höschele, and K. Ruck, *Chem. Ber.*, 1953, **86**, 1277.

water, was chromatographed on a column (45 cm. × 2·1 cm.) of Dowex-1 (OH^-) resin and material was eluted with water, the eluate being collected in fractions (15 ml.). Fractions 27—35 contained 2-*O*-D-galactosyl-D-erythritol; fractional crystallisation from aqueous ethanol gave the *α-anomer* (0·06 g.), m. p. 150—151°, $[\alpha]_D$ +146° (*c* 0·4 in water) (Found: C, 42·4; H, 7·1. $C_{10}H_{20}O_9$ requires C, 42·25; H, 7·1%). The residue obtained on evaporation of the ethanolic mother-liquors was acetylated and fractional crystallisation of the product from ethanol gave the *hepta-*O*-acetyl derivative* of the α-anomer (0·37 g.), m. p. 114°, $[\alpha]_D$ +109° (*c* 0·6 in acetone) (Found: C, 50·1; H, 6·25. $C_{24}H_{34}O_{16}$ requires C, 49·8; H, 6·0%). Evaporation of these ethanolic mother-liquors to dryness gave a syrupy acetate which on catalytic deacetylation with sodium methoxide in methanol was converted into 2-*O*-β-D-galactosyl-D-erythritol (0·08 g.) which on recrystallisation from aqueous ethanol had m. p. 179—181°, $[\alpha]_D$ +7·3° (*c* 0·6 in water) (Found: C, 42·4; H, 6·9. Calc. for $C_{10}H_{20}O_9$: C, 42·25; H, 7·1%); Charlson *et al.*[8] give m. p. 184—187°, $[\alpha]_D$ +7°. The m. p. of this compound was not depressed on mixing it with material, m. p. 180°, obtained by Dr. D. A. Kennedy from a Smith degradation [9] of *Pneumococcus* type 11A capsular substance, and the infrared spectra of the two were indistinguishable.

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