414. *Synthesis of* 4-O-(β-D-*Glucopyranosyl*)-D-*ribitol, a Degradation Product of the Ribitol Teichoic Acid from the Walls of* Bacillus subtilis.

By J. Baddiley, J. G. Buchanan, and F. E. Hardy.

4-*O*-(β-D-Glucopyranosyl)-D-ribitol, a degradation product of the teichoic acid from *Bacillus subtilis* walls, has been synthesised by a Koenigs–Knorr reaction from tetra-*O*-acetyl-α-D-glucopyranosyl bromide and 5-*O*-benzyl-2,3-*O*-isopropylidene-1-*O*-triphenylmethyl-D-ribitol. Evidence is presented that no migration of protecting groups occurred during the synthesis, and an explanation is offered for a migration observed in a synthesis of *O*-galactosyl-glycerols.

Teichoic acids, polymeric esters of phosphoric acid, are present in the walls and cell contents of a number of bacteria.[1-4] Hydrolysis of the wall teichoic acid from *Bacillus subtilis* with alkali, followed by enzymic dephosphorylation, gives 4-*O*-(β-D-glucopyranosyl)-D-ribitol.* On the basis of this and other evidence, a structure has been assigned to the teichoic acid.[5,6] A synthesis of the phosphorus-free degradation product was desirable.

Since the glucoside has a β-configuration, a possible synthesis entails reaction between

* Equivalent name: 2-*O*-(β-D-glucopyranosyl)-L-ribitol. Cf. *J.*, 1957, 1870, footnote.

[1] Armstrong, Baddiley, Buchanan, Carss, and Greenberg, *J.*, 1958, 4344.
[2] Baddiley, *Proc. Chem. Soc.*, 1959, 177.
[3] Armstrong, Baddiley, Buchanan, Davison, Kelemen, and Neuhaus, *Nature*, 1959, **184**, 247.
[4] Baddiley and Davison, *J. Gen. Microbiol.*, 1961, **24**, 295.
[5] Armstrong, Baddiley, and Buchanan, *Nature*, 1959, **184**, 248.
[6] Armstrong, Baddiley, and Buchanan, *Biochem. J.*, 1960, **76**, 610.

tetra-*O*-acetyl-α-D-glucopyranosyl bromide and a suitably protected ribitol derivative.[7,8] Koenigs–Knorr reactions between glycosyl halides and secondary alcohols do not normally give high yields of the required glycosides; nevertheless, the method has been used in rational syntheses of several disaccharides.[7,9,10] The required derivative of ribitol should have only the 4-hydroxyl group (D-form) free. Since ribitol itself is a *meso*-form it was necessary to use as starting material an optically active derivative, such as D-ribose or D-ribonolactone. A similar situation arose in the synthesis of cytidine diphosphate ribitol and its degradation products.[11]

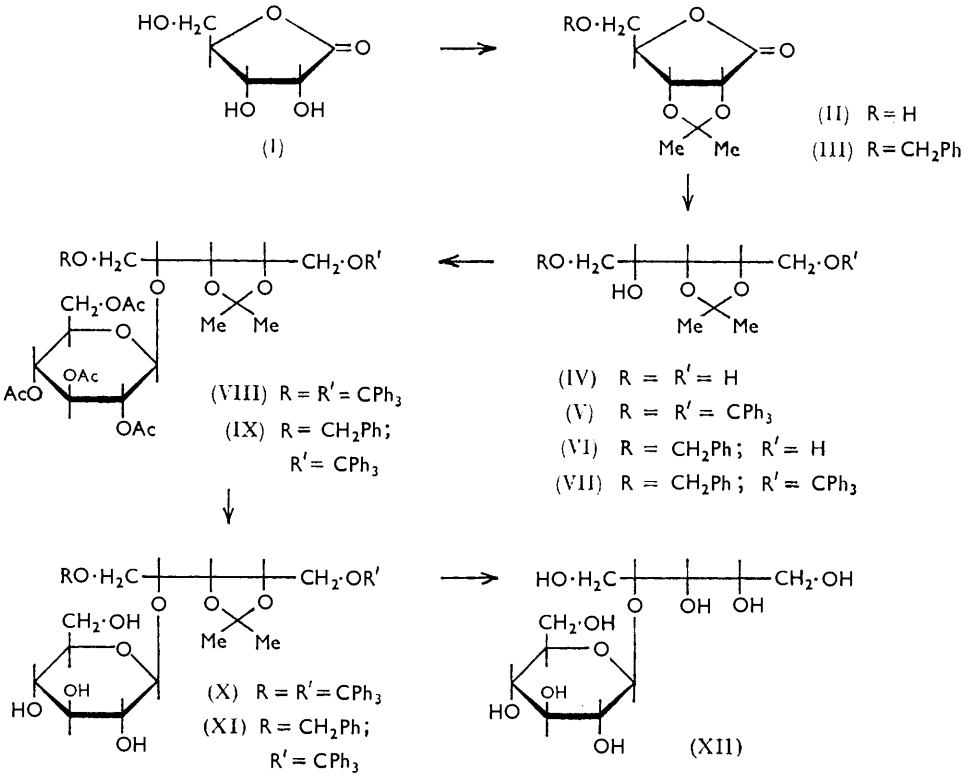
D-Ribonolactone (I) was converted into 2,3-*O*-isopropylidene-D-ribitol (IV) by reduction of the isopropylidene-lactone (II) with lithium aluminium hydride.[12] Triphenylmethylation gave the crystalline 1,5-di-*O*-triphenylmethyl ether (V), further characterised as its crystalline 4-benzoate. Condensation of tetra-*O*-acetylglucosyl bromide with the ether (V) in benzene solution in the presence of silver carbonate, iodine, and anhydrous calcium sulphate, gave a product which was deacetylated catalytically in methanol. The crystalline starting material (V) was recovered in 76% yield. The remaining product was partitioned between water and chloroform to extract water-soluble compounds, and the chloroform-soluble portion, presumably containing the glucoside (X), was hydrolysed with acid to remove triphenylmethyl and isopropylidene groups. Paper chromatography showed the presence of ribitol and two compounds having R_F values close to that of the required glucoside. Chromatography on charcoal–Celite gave a fraction containing the two monoglucosides free from other material. This mixture had the following properties: (*a*) one component had an R_F value identical with that of the glucoside from the teichoic acid; (*b*) the mixture was completely hydrolysed to ribitol and glucose by a crude emulsin preparation known not to hydrolyse α-glucosides; (*c*) the mixture, after successive oxidation with sodium periodate, reduction with sodium borohydride, and hydrolysis with acid, gave both ethylene glycol and glycerol.[13] It appeared, therefore, that the synthesis had yielded small amounts of D-ribitol 4-β-D-glucoside and D- or L-ribitol 1-β-D-glucoside. The latter must have arisen through loss of one or other of the two triphenylmethyl groups during the condensation. Such a reaction has been used recently by Bredereck and his co-workers in the synthesis of disaccharides from triphenylmethyl ethers and glycosyl halides in the presence of silver perchlorate.[14] Under the conditions used here loss of a triphenylmethyl group with simultaneous glycosylation might be favoured through steric hindrance of the 4-hydroxyl group in the ether (V) by the bulky triphenylmethyl group at the 5-position.

Three points were clear from the unsuccessful synthesis: (i) β-glucosides were formed; (ii) the isopropylidene group was retained throughout the condensation, since no 3-glucoside, which would be readily detected on chromatograms by its yellow colour with the periodate–Schiff reagents,[15] was found; (iii) no acid-catalysed migration of isopropylidene group had taken place, since the recovered starting material retained its full optical activity. In view of the limited success of these experiments it was decided to prepare the *O*-benzyl ether (VII), and to examine its reaction with the glucosyl bromide.

The *O*-isopropylideneribonolactone (II) was treated with benzyl bromide and silver oxide in dimethylformamide according to Croon and Lindberg's procedure.[16] Hough, Jones, and Mitchell [12] have shown that methylation of this lactone by Purdie's method gave the 5-*O*-methyl ether without opening of the lactone ring. The benzyl ether was

[7] Evans, Reynolds, and Talley, *Adv. Carbohydrate Chem.*, 1951, **6**, 27.
[8] Haynes and Newth, *Adv. Carbohydrate Chem.*, 1955, **10**, 207.
[9] Bächli and Percival, *J.*, 1952, 1244.
[10] Aspinall and Ferrier, *J.*, 1958, 1501.
[11] Baddiley, Buchanan, and Fawcett, *J.*, 1959, 2192.
[12] Hough, Jones, and Mitchell, *Canad. J. Chem.*, 1958, **36**, 1720.
[13] Viscontini, Hoch, and Karrer, *Helv. Chim. Acta*, 1955, **38**, 642.
[14] Bredereck, Wagner, Faber, Ott, and Rauther, *Chem. Ber.*, 1959, **92**, 1135.
[15] Archibald, Baddiley, and Buchanan, *Biochem. J.*, in the press.
[16] Croon and Lindberg, *Acta Chem. Scand.*, 1959, **13**, 593.

purified by chromatography on silica and the resulting syrup, which was homogeneous on paper chromatography, was purified further by distillation; it was characterised as the crystalline cyclohexylamide. Reduction by lithium aluminium hydride afforded the *O*-benzylribitol (VI) as a chromatographically homogeneous syrup; hydrogenolysis of the latter gave a single compound shown by chromatography to be 2,3-*O*-isopropylideneribitol (IV). Triphenylmethylation of the ether (VI) gave the required benzyl triphenylmethyl ether (VII), conveniently isolated as its 4-acetate and regenerated therefrom by deacetylation.



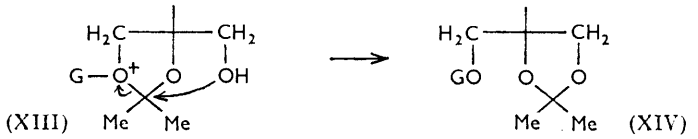
The Koenigs–Knorr reaction was carried out as before giving, after deacetylation and chromatography on neutral alumina, a solid with the properties of the *O*-benzyl-*O*-glucosyl-*O*-isopropylidene-*O*-triphenylmethylribitol (XI) in 7·5% yield. Removal of protecting groups by hydrogenolysis and acid-hydrolysis gave 4-*O*-(β-D-glucopyranosyl)-D-ribitol (XII), identical with that obtained from the *B. subtilis* teichoic acid.[5,6]

The infrared spectrum of the synthetic glucoside, which had crystallised from anhydrous methanol–ether, differed appreciably from that of the glucoside from the teichoic acid.[6] The latter glucoside has since been found [17] to be a hemihydrate, and when it was recrystallised from methanol–ether the infrared spectra of the synthetic and the "natural" compound were identical. The spectrum of the hemihydrate shows a characteristic hydrate maximum [18] at 1634 cm.$^{-1}$, and Dr. Lewis J. Sargent in this laboratory has found similar differences in the infrared spectra of crystalline cellobiitol and its hydrate when measured from KBr discs. Comparison was made of m. p.s, infrared spectra and specific rotation of

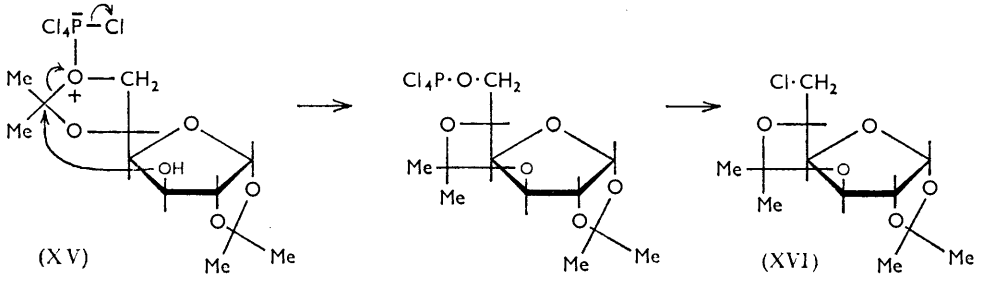
[17] Armstrong, Baddiley, and Buchanan, *Biochem. J.*, in the press.
[18] Colbran, Guthrie, and Parsons, *J.*, 1960, 3532.

the glucosides and their crystalline octa-acetates. Paper chromatograms of the glucosides and their partial acid-hydrolysates were identical.

In the second synthesis there was no indication of the formation of a 1-*O*-glucosylribitol derivative. However, it is possible that traces of this compound and a corresponding amount of triphenylmethanol were formed,[14] the former being lost during washing of chloroform solutions with water.



In a Koenigs–Knorr reaction in chloroform, with silver oxide in the place of silver carbonate, Wickberg[19] observed apparent isomerisation of optically active 1,2-*O*-isopropylidene-L-glycerol due to migration of the isopropylidene group. In reaction with



tetra-*O*-acetyl-α-D-galactopyranosyl bromide both 1-L- and 1-D-glycerol isomers were produced. We have obtained no evidence for such isomerisation in our reactions. In the first synthesis through the di-*O*-triphenylmethyl ether (V) the recovered starting material had unaltered optical activity; acid-catalysed migration of the isopropylidene residue would have caused racemisation. In the second synthesis, some of the starting material (VII) which was recovered by chromatography was hydrogenolysed and triphenylmethylated. The resulting ether (V) possessed the correct optical activity, and therefore we are confident that the synthetic glucoside is the 4-*O*-glucosyl-D-ribitol isomer.

The extensive racemisation observed by Wickberg[19] may be related to his isopropylidene compound's being derived from a primary alcohol. By a mechanism similar to that proposed for the acetolysis of acetals,[20] the co-ordination of the carbonium ion (G^+) derived from the glycosyl halide to the ketal-oxygen atom can be envisaged as in (XIII) ⟶ (XIV). This would proceed in addition to the normal Koenigs–Knorr glycosylation of the free hydroxyl group and lead to the formation of a mixture of isomers. In the ribitol derivatives (V) and (VII) both ketal-oxygen atoms are relatively hindered and so could not easily form similar co-ordination compounds. This view was confirmed by acetylation of the mother-liquors from crystallisation of the synthetic glucosylribitol; only the octa-acetate previously prepared from a crystalline sample of the glucoside was detected.

A similar mechanism may explain the formation of 6-chloro-6-deoxy-1,2:3,5-di-*O*-isopropylidene-α-D-glucose (XVI) from 1,2:5,6-di-*O*-isopropylidene-α-D-glucose (XV) and phosphorus pentachloride.[21]

This scheme seems preferable to that proposed by Smith.[21]

[19] Wickberg, *Acta Chem. Scand.*, 1958, **12**, 1187.
[20] Bourne, Burdon, and Tatlow, *J.*, 1958, 1274; 1959, 1864.
[21] Smith, *J.*, 1956, 1244.

Experimental

Infrared spectra were determined on potassium bromide discs. Silica gel (British Drug Houses) or neutral alumina (Grade O alumina neutralised with acetic acid and reactivated) were used for chromatography.

Paper Chromatography.—Whatman No. 1 or No. 4 paper was used. The following solvent systems were used by descending irrigation: (A) Butan-1-ol–ethanol–water (5 : 1 : 4). (B) Butan-1-ol–ethanol–water–ammonia (*d* 0·88) (40 : 10 : 49 : 1).[22] (C) Butan-1-ol–ethanol–water (4 : 1 : 1). (D) Di-isopropyl ether on paper treated with dimethyl sulphoxide.[23] (E) Light petroleum (b. p. 60—80°) on paper treated as in (D).[23]

All compounds containing α-glycol groups were detected with the periodate–Schiff reagents,[24] and those containing isopropylidene groups by the periodic acid–Schiff reagents.[25] Triphenylmethyl ethers were detected with perchloric acid.[26]

2,3-O-*Isopropylidene*-D-*ribitol.*—This was prepared from D-ribonolactone.[12] It was chromatographically homogeneous in solvent A (R_F 0·71), and gave ribitol and anhydroribitol on acid hydrolysis.

2,3-O-*Isopropylidene*-1,5-*di*-O-*triphenylmethyl*-D-*ribitol.*—The above acetal (0·75 g.) was treated with triphenylmethyl chloride (2·6 g., 2·4 mol.) in pyridine (5 c.c.) for 3 days at room temperature. Isolated by use of chloroform, and crystallised from ethanol, the *ether* (2·1 g., 80%) had m. p. 170—171°, $[\alpha]_D^{24}$ +17·2° (*c* 4·1 in C_6H_6) (Found: C, 81·3; H, 6·7. $C_{46}H_{44}O_5$ requires C, 81·7; H, 6·5%). In solvent E it had R_F 0·88 (triphenylmethanol had R_F 0·23). It gave a crystalline *benzoate*, m. p. 87—89° from ethanol, when treated with benzoyl chloride in pyridine (Found: C, 81·2; H, 6·1. $C_{53}H_{48}O_6$ requires C, 81·6; H, 6·2%).

Koenigs–Knorr Reaction with 2,3-O-*Isopropylidene*-1,5-*di*-O-*triphenylmethyl*-D-*ribitol.*—The above ether (1·44 g.) was dissolved in pure, dry benzene (15 c.c.), anhydrous calcium sulphate (heated at 240—270° for 2·5 hr.; 3·5 g.) and silver carbonate (1·5 g.) were added, and the mixture was shaken vigorously for 12 hr. Iodine (0·2 g.) was added and a solution of tetra-*O*-acetyl-α-D-glucopyranosyl bromide (0·9 g., 1·03 mol.) in benzene (7 c.c.) was introduced during 30 min. with constant shaking in the dark. The shaking, with occasional release of carbon dioxide from the flask, was continued for 80 hr.[9] The mixture was filtered through "Hyflo Supercel" silica, and the filtrate extracted twice with water and evaporated to dryness. The residue was dissolved in methanol (25 c.c.), sodium methoxide (from 0·015 g. of sodium) in methanol (15 c.c.) added, and the mixture shaken for 6 hr. The crystals which separated (1·0 g.) were filtered off and identified as starting material (V) by specific rotation, $[\alpha]_D^{22}$ +17·1° (*c* 5·0 in C_6H_6), m. p., and infrared spectra. The filtrate was neutralised (solid carbon dioxide) and evaporated to dryness. The residue was shaken with a mixture of chloroform and water. Evaporation of the chloroform layer gave a syrup (0·5 g.) which was heated under reflux with acetone (50 c.c.) containing 2N-sulphuric acid (1·5 c.c.) for 4 hr. Water (20 c.c.) and 2N-sulphuric acid (1 c.c.) were added and heating was continued for 1 hr. The solution was neutralised by barium carbonate, and triphenylmethanol precipitated by addition of water. After filtration, the solution was evaporated to a syrup (0·15 g.). Chromatography in solvent B showed a complex mixture containing mainly ribitol and two components with R_F values in the ribitol monoglucoside region. The faster spot had the same $R_{ribitol}$ (0·58) as the glucoside from the teichoic acid; the slower spot had $R_{ribitol}$ 0·50. This crude product was chromatographed on a carbon–Celite column (from 12 g. of Norit A and 7 g. of Celite-545).[27] Elution with 5% ethanol gave a chromatographically pure syrup (0·02 g.) containing the two glucosides.

Action of β-*Glucosidase.*—A sample (1 mg.) of the above mixture in water (30 μl.) was incubated with a 1% solution of β-glucosidase (L. Light and Co.) (30 μl.) at 37° for 3 days under toluene. Chromatography of the product in solvent B showed that both glucosides had been completely hydrolysed and that the only products were glucose and ribitol.

Periodate Oxidation and Borohydride Reduction.[13]—The above ribitol glucosides (1·7 mg.)

[22] Hirst, Hough, and Jones, *J.*, 1949, 928.
[23] Wickberg, *Acta Chem. Scand.*, 1958, **12**, 615.
[24] Baddiley, Buchanan, Handschumacher, and Prescott, *J.*, 1956, 2818.
[25] Buchanan, Dekker, and Long, *J.*, 1950, 3162.
[26] Applegarth and Buchanan, *J.*, 1960, 4706.
[27] Zilliken, Rose, Braun, and Gyorgy, *Arch. Biochem. Biophys.*, 1955, **54**, 392.

and sodium metaperiodate (9 mg.) were dissolved in water (0·1 c.c.) and kept in the dark overnight. Sodium borohydride (10 mg.) was added and the solution kept overnight. 3N-Hydrochloric acid (0·1 c.c.) was added and the solution was boiled for 15 min. The product was chromatographed on paper in ethyl acetate–pyridine–water (7 : 2 : 1). Two spots with R_F 0·43 and 0·55, corresponding to glycerol and ethylene glycol respectively, were observed when the paper was sprayed with the periodate–Schiff reagents.

5-O-*Benzyl*-2,3-O-*isopropylidene*-D-*ribono*-1,4-*lactone*.—2,3-*O*-Isopropylidene-D-ribonolactone (1 g.) was dissolved in anhydrous dimethylformamide (30 c.c.), and purified benzyl bromide (5·5 c.c.) was added. Silver oxide (6 g.) was introduced during 60 min. with vigorous stirring which was continued for 16 hr. (cf. ref. 16). The mixture was filtered, the brown residue being washed with dimethylformamide (25 c.c.) and then chloroform (25 c.c.), and 1% potassium cyanide solution (250 c.c.) was added to the combined filtrate. The mixture was extracted with chloroform (3 × 50 c.c.), and the chloroform solution washed with water, dried (Na_2SO_4), and evaporated to a syrup. Most of the excess of benzyl bromide was removed by distillation at 90°/0·05 mm. Last traces were removed by quaternisation with pyridine (3·5 c.c.) overnight. The product was re-isolated with chloroform to give a syrup (2·2 g.) which was chromatographed on silica gel (60 g.). Benzene eluted dibenzyl ether and benzaldehyde, and benzene–ether eluted the required *lactone* (1·4 g.), which was homogeneous by paper chromatography. It was distilled at 125—135° (bath-temp.)/10^{-5} mm. and had n_D^{22} 1·5065, $[\alpha]_D^{23}$ −39·6° (*c* 1·1 in EtOH) (Found: C, 64·6; H, 6·6. $C_{15}H_{18}O_5$ requires C, 64·8; H, 6·5%). In solvent C, it had R_F 0·96 (ribonolactone had R_F 0·42; 2,3-*O*-isopropylideneribonolactone had R_F 0·80).

The lactone (0·34 g.) was treated with cyclohexylamine (2·5 c.c.) at 100° for 2 hr. and then at 50° overnight (cf. ref. 28). The *cyclohexylamide*, m. p. 63—65°, was isolated by using chloroform and crystallised from light petroleum (b. p. 60—80°) (Found: C, 66·8; H, 8·4. $C_{21}H_{31}O_5N$ requires C, 66·9; H, 8·2%).

5-O-*Benzyl*-2,3-O-*isopropylidene*-D-*ribitol*.—The preceding lactone (1 g.) in tetrahydrofuran (17 c.c.) was added dropwise to a suspension of lithium aluminium hydride (0·5 g.) in tetrahydrofuran (17 c.c.). The mixture was heated under reflux for 8 hr. Ethyl acetate (2 c.c.) was added with cooling and stirring, followed by 90% ethanol (75 c.c.). The precipitate was removed by centrifugation and washed with two volumes of ethanol. The combined centrifugates were evaporated to dryness and the residue was extracted with hot chloroform (3 × 70 c.c.). The combined chloroform solutions were washed with water, dried, and evaporated to a syrup (1 g.) which was chromatographically homogeneous (R_F 0·90 in solvent A).

The benzyl ether (0·1 g.) was hydrogenated for 20 hr. over palladium (from 0·1 g. of oxide) in ethanol (20 c.c.). Chromatography in solvent A showed that 2,3-*O*-isopropylideneribitol was the only product.

4-O-*Acetyl*-5-O-*benzyl*-2,3-O-*isopropylidene*-1-O-*triphenylmethyl*-D-*ribitol*.—5-*O*-Benzyl-2,3-*O*-isopropylidene-D-ribitol (0·75 g.) was treated with triphenylmethyl chloride (0·8 g., 1·05 mol.) in pyridine (5 c.c.) for 4 days at room temperature. The syrupy product (1·5 g.) was isolated in the same way as the previous di-*O*-triphenylmethyl ether. When examined on paper in solvent D it was found to contain triphenylmethanol together with a major component with $R_{\text{triphenylmethanol}}$ (written R_t below) 1·25. The syrup was acetylated with acetic anhydride (7 c.c.) in pyridine (10 c.c.), and the products were isolated by using benzene. When crystallised from ethanol the *acetate* (0·8 g., 54%) had m. p. 112—114° (Found: C, 76·6; H, 7·0. $C_{36}H_{38}O_6$ requires C, 76·3; H, 6·7%).

5-O-*Benzyl*-2,3-O-*isopropylidene*-1-O-*triphenylmethyl*-D-*ribitol*.—The above acetate (0·32 g.) was deacetylated catalytically with sodium methoxide in methanol. Crystallisation from aqueous methanol gave the *ether* (0·28 g.), m. p. 52—54°. Recrystallised from methanol it had m. p. 53—55°, $[\alpha]_D^{22}$ +20·3° (*c* 4·1 in C_6H_6) (Found: C, 75·6; H, 7·1. $C_{34}H_{36}O_5,CH_3{\cdot}OH$ requires C, 75·5; H, 7·2%). This compound could not be crystallised from acetone or acetone–water. In solvent D it had R_t 1·25 and in E it had R_F 0·73 (triphenylmethanol had R_F 0·23).

Koenigs–Knorr Reaction with 5-O-*Benzyl*-2,3-O-*isopropylidene*-1-O-*triphenylmethyl*-D-*ribitol*.—The last-mentioned ether (2·0 g.) was treated with tetra-*O*-acetyl-α-D-glucopyranosyl bromide (1·8 g., 1·15 mol.) in benzene (30 c.c.) in the presence of silver carbonate (3·0 g.), anhydrous calcium sulphate (7·0 g.), and iodine (0·35 g.), the technique being the same as before.

[28] Baddiley and Thain, *J.*, 1951, 246.

The product was deacetylated as before and, after neutralisation with solid carbon dioxide, was evaporated to dryness. A chloroform solution of the residue was washed with water and then saturated sodium chloride solution, then it was dried (K_2CO_3) and evaporated to a syrup (1·9 g.). Paper chromatography in solvent D showed the presence of three triphenylmethyl derivatives: a small amount of triphenylmethanol, a major quantity of starting material, and a compound with R_F 0·01. The mixture was chromatographed on neutral alumina (90 g.). Benzene and benzene–chloroform eluted the first two components; elution with chloroform–methanol (95 : 5) gave the third component (XI) (0·2 g., 7·5%) chromatographically pure, that crystallised (m. p. 80—82°) when triturated with light petroleum.

4-O-(β-D-*Glucopyranosyl*)-D-*ribitol*.—The above glucoside (0·2 g.) was hydrogenated over palladium (from 0·4 g. of oxide) in ethanol (40 c.c.) at atmospheric pressure for 60 hr. After removal of catalyst the solution was evaporated to dryness and the residue was heated in ethanol (47·5 c.c.) and N-sulphuric acid (2·5 c.c.) for 45 min. The solution was neutralised with barium carbonate and passed through Dowex-50 (NH_4^+) resin. After evaporation, the residue was shaken with water and chloroform, and the aqueous layer was examined chromatographically in solvent B. Only one compound was detected, having the same mobility as the glucoside from the *B. subtilis* teichoic acid. A mixture of the two ran as a single spot. The synthetic glucoside was purified further on a carbon–Celite column prepared from Norit A (20 g.) and Celite-545 (10 g.). Elution with 6% ethanol and evaporation gave the glucoside (0·06 g.). This was dissolved in a little methanol and ether was added to turbidity. The crystalline glucoside (0·02 g.), $[\alpha]_D^{22}$ −22° (*c* 1·0 in H_2O) had m. p. 134—137°, undepressed in admixture with the natural glucoside [6,17] (Found: C, 41·6; H, 7·0. Calc. for $C_{11}H_{22}O_{10}$: C, 42·0; H, 7·1%). The infrared spectra of the synthetic compound and the natural glucoside (which had been crystallised in the same way) were indistinguishable.

Acid Hydrolysis.—Samples (1·0 mg.) of the two glucosides were hydrolysed with 2N-hydrochloric acid at 100° for 9 hr. The hydrolysates were evaporated to dryness and chromatographed in solvent B. The hydrolysis products were identical, anhydroribitol, ribitol, glucose, and small amounts of acid-reversion products being detected.

4-O-(β-D-*Glucopyranosyl*)-D-*ribitol Octa-acetate*.—The glucoside (0·03 g.) was added to a mixture of acetic anhydride (1·5 c.c.) and pyridine (1·5 c.c.). After 2 days at room temperature the *acetate* was isolated with chloroform. It crystallised from ethanol or ether–light petroleum (b. p. 40—60°) as needles, m. p. 100°, $[\alpha]_D^{22}$ −14·1° (*c* 1·5 in $CHCl_3$) (Found: C, 49·7; H, 6·2. $C_{27}H_{38}O_{18}$ requires C, 49·8; H, 5·9%). The acetates derived from the synthetic and natural glucosides had the same m. p., were undepressed in admixture, possessed identical infrared spectra, and gave identical analytical figures.

Conversion of 5-O-*Benzyl*-2,3-O-*isopropylidene*-1-O-*triphenylmethyl*-D-*ribitol recovered from the Koenigs–Knorr Reaction into* 2,3-O-*Isopropylidene*-1,5-*di*-O-*triphenylmethyl*-D-*ribitol*.—The recovered syrupy starting material (VII) (0·35 g.) was hydrogenated in ethanol (35 c.c.) over palladium (from 0·6 g. of oxide) at atmospheric pressure for 24 hr. After filtration and evaporation the residue was treated with triphenylmethyl chloride (0·3 g.) in pyridine (4 c.c.) for 4 days. Isolated with chloroform, the syrupy product was chromatographed on alumina. Elution with chloroform gave a syrup (0·28 g.) which crystallised from methanol–water. It had m. p. 170—171°, $[\alpha]_D^{22}$ +17·5° (*c* 3·0 in C_6H_6). Its infrared spectrum was identical with that of the compound (V) prepared earlier.

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Department of Chemistry, King's College,
University of Durham, Newcastle upon Tyne. [*Received, December 21st*, 1960.]