Carbohydrate Research, 70 (1979) 37–46
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SYNTHESIS OF THE REPEATING UNIT OF THE TEICHOIC ACID ISOLATED FROM THE CELL WALL OF *Bacillus subtilis* VAR. *niger* WM*

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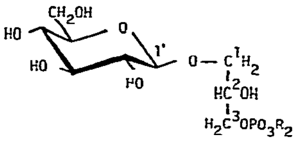
(Received March 17th, 1978; accepted for publication, April 22nd, 1978)

ABSTRACT

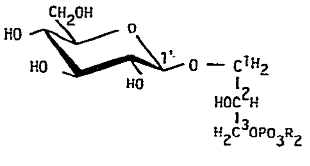
Stereocontrolled synthesis of 1-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3-*O*-isopropylidene-D-glycerol (**6**) was achieved in good yield by use of the modified, orthoester method. Compound **6** was then transformed into 1-deoxy-3-*O*-phosphono-D-glycerol-1-yl β-D-glucopyranoside (**1**), identical with the repeating unit of the teichoic acid isolated from the cell wall of *Bacillus subtilis* var. *niger* WM, in a regio-controlled way, unambiguous evidence for the assignment of the stereochemistry of the natural product being provided by the ^{13}C-n.m.r. data for **1** and its L-glycerol-1-yl isomer.

INTRODUCTION

In 1976, the structure of the repeating unit of the teichoic acid isolated from the cell wall of *Bacillus subtilis* var. *niger* WM was reported by DeBoer *et al.*[1] to be **1**. However, the stereochemistry of the glycerol moiety remained to be assigned, owing to lack of reference compounds for ^{13}C-n.m.r. studies. We report here a stereo- and regio-specific synthesis of the target molecules **1** and its L-glycerol-1-yl isomer (**2**), which provide unambiguous evidence for the assignment of the stereochemistry of the glycerol residue of the natural product as being 1-deoxy-D-glycerol-1-yl (3-deoxy-*sn*-glycerol-3-yl)†.



1 R = H
13 R = Na



2 R = H
19 R = Na

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*Taken from a part of the Ph. D. thesis of K. K.
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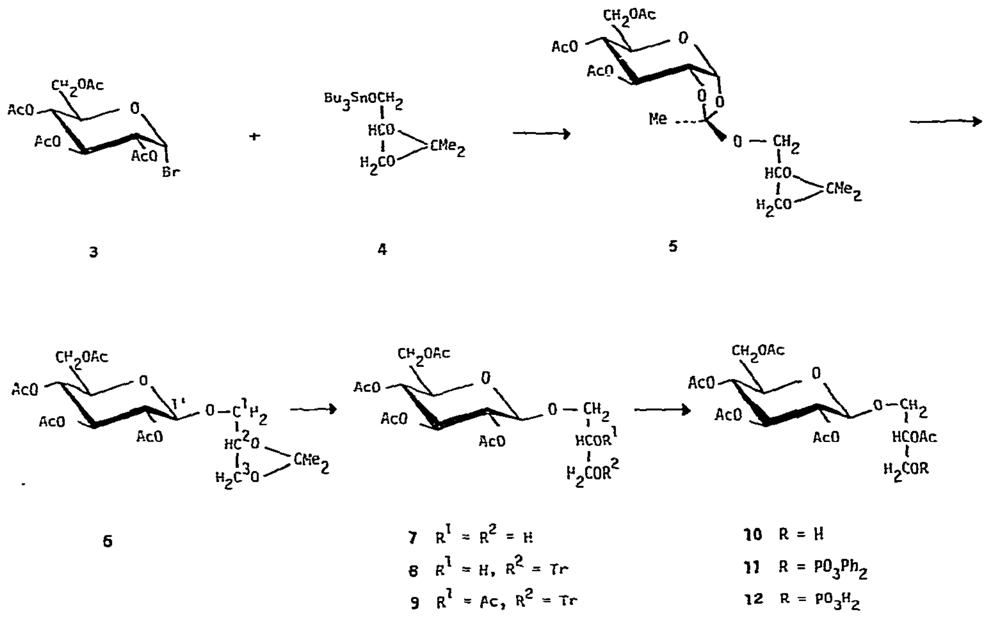
†The biochemical nomenclature, in which all asymmetrically substituted glycerol residues are regarded as being those of L-glycerol, and called *sn*-glycerol residues, was found unsuitable for use in this work.

RESULT AND DISCUSSION

Even though the Koenigs–Knorr method for the synthesis of glycerol glycosides was reported to be unsuitable for control of the stereochemistry with a glycerol residue that carries an isopropylidene group[2], stereocontrolled synthesis of glycerol D-glucosides by use of the orthoester approach has been performed, although in only moderate yields[3].

In order to obtain derivatives of 1-*O*-β-D-glucopyranosyl-D-glycerol in an efficient way, direct orthoester approach[4] by use of tributyltin alkoxide was examined. A stoichiometric mixture of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**3**) and 2,3-*O*-isopropylidene-1-*O*-(tributyltin)-D-glycerol (**4**), readily prepared from the corresponding alcohol[5], in 1,2-dichloromethane was heated at 55° in the presence of added tetraethylammonium bromide to give, stereospecifically, the *exo*-orthoester **5** in 87% yield. The *exo*-stereochemistry of **5** was assigned from the presence of a signal for C-Me at δ 1.72 in the ^{1}H-n.m.r. spectrum[4], in accordance with the ^{1}H-n.m.r. data discussed by Lemieux and Morgan[6]. Subsequent treatment of **5** with mercuric bromide, without a solvent, at 135° afforded the rearranged[7], 1,2-*trans*-D-glucoside **6** in 75% yield.

As stereocontrolled D-glucosylation at the 1-hydroxyl group of protected D-glycerol could be achieved in a satisfactory yield, the product **6** was then submitted to the well established sequence of reactions shown in Scheme 1. Treatment with 20% aq. acetic acid during 70 min at 100° gave a 65% yield of diol **7**. Tritylation of **7** and acetylation of the ether **8** afforded trityl acetate **9**, which was further converted



3 4 5

6

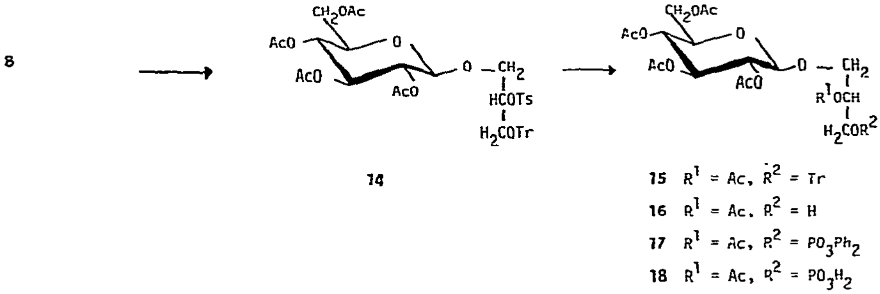
7 $R^1 = R^2 = H$
8 $R^1 = H$, $R^2 = Tr$
9 $R^1 = Ac$, $R^2 = Tr$

10 R = H
11 $R = PO_3Ph_2$
12 $R = PO_3H_2$

Scheme 1.

into the diphenylphosphate **11** by two successive reactions: (*a*) detritylation with 80% aq. acetic acid during 1 h at 50°, to give **10**, and (*b*) treatment with diphenylphosphorochloridate in pyridine at room temperature to give **11**. Hydrogenolysis of **11** with hydrogen in the presence of platinum oxide gave **12**, and deacetylation of **12** gave sodium salt **13** as an amorphous solid, m.p. 159–165°, $[\alpha]_D$ −17.3° (*c* 0.56, H_2O), in a 30% overall yield from **6**.

Synthesis of 1-*O*-*β*-D-glucopyranosyl-3-*O*-phosphono-L-glycerol disodium salt **19** was achieved by epimerization of C-2 of the glycerol residue of **8**. The *p*-toluenesulfonate **14**, prepared from **8** in 77% yield, was treated with potassium acetate and dibenzo-18-crown-6, to afford the trityl acetate **15** in 60% yield. Subsequent transformation of **15** into **19**, m.p. 133–141°, $[\alpha]_D$ −28.9° (*c* 0.53, H_2O), was achieved in 32% yield by taking the same route as for the transformation of **9** into **13** (see Scheme 2).



Scheme 2.

^{13}C-N.m.r. data were acquired both for the disodium phosphates (**13** and **19**), and the dihydrogenphosphates (**1** and **2**). The spectra are shown in Figs. 1 and 2. The clear difference between the ^{13}C-n.m.r. spectra of **13** and **19** with respect to the relative chemical-shifts of the signals for C-2 and C-4′ in each compound must be due to the difference of stereochemistry at C-2 of the glycerol residue (see Fig. 1). This, in turn, should be diagnostic for assignment of the stereochemistry of the natural product*. It is to be noted, however, that neither the ^{13}C-n.m.r. data for **1** and **2** (see Fig. 2), nor those for 1-*O*-*β*-D-glucosyl-D-glycerol** and 1-*O*-*β*-D-glucosyl-L-glycerol** (see Fig. 3), showed any noticeable difference that would be diagnostic for the stereochemical assignment for the glycerol residues.

As it has been proposed[1] that the phosphono group of **1** is linked to O-2 of the glycerol residue of the adjacent repeating unit **1** in the teichoic acid, the bisphosphate **21** was synthesized as a model compound for ^{13}C-n.m.r. studies. Treatment of **7** with an excess of diphenylphosphorochloridate resulted in the formation of **20** in 19% yield. Subsequent hydrogenolysis, and deacetylation, afforded the tetrasodium salt **21**, $[\alpha]_D$ −14.8° (*c* 0.41, H_2O); the ^{13}C-n.m.r. data for **21** are given in Fig. 4.

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*Prof. W. R. DeBoer confirmed the identity of the natural sample with the sample of synthetic **1** (in a personal communication to the authors).

These compounds were prepared by deacetylation of **7 and **16**, respectively.

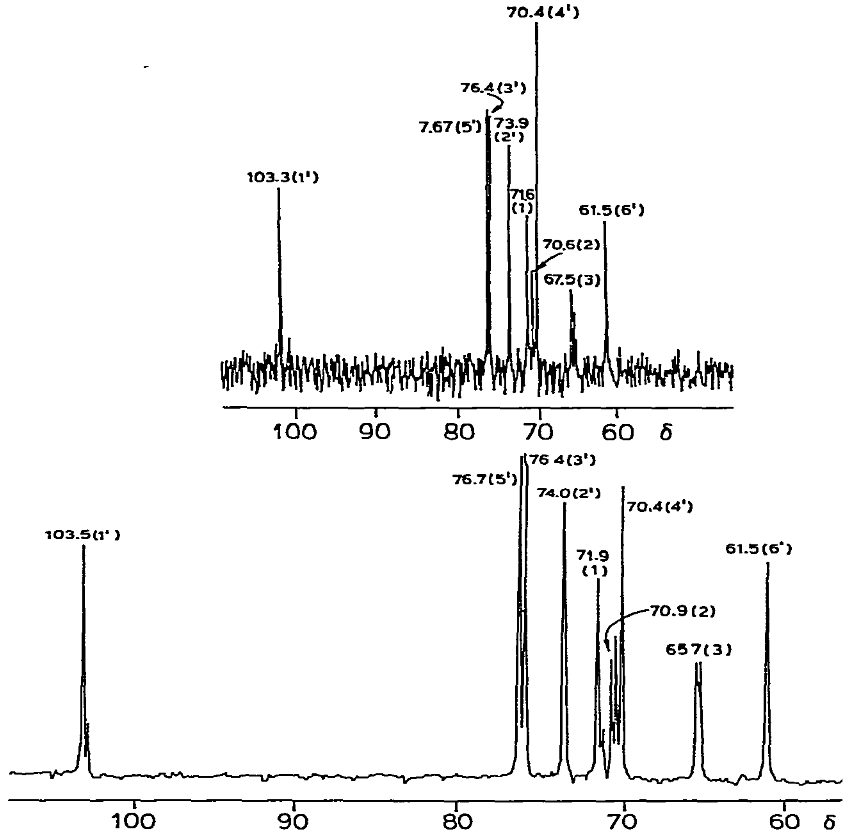


Fig. 1. ^{13}C-N.m.r. spectra of synthetic **13** (above) and **19** (below) in D_2O.

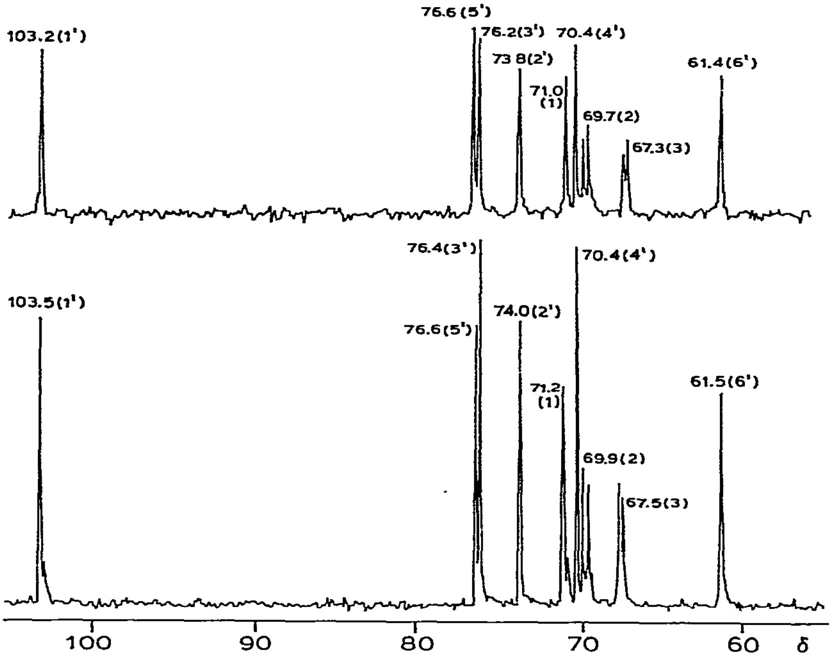


Fig. 2. ^{13}C-N.m.r. spectra of synthetic **1** (above) and **2** (below) in D_2O.

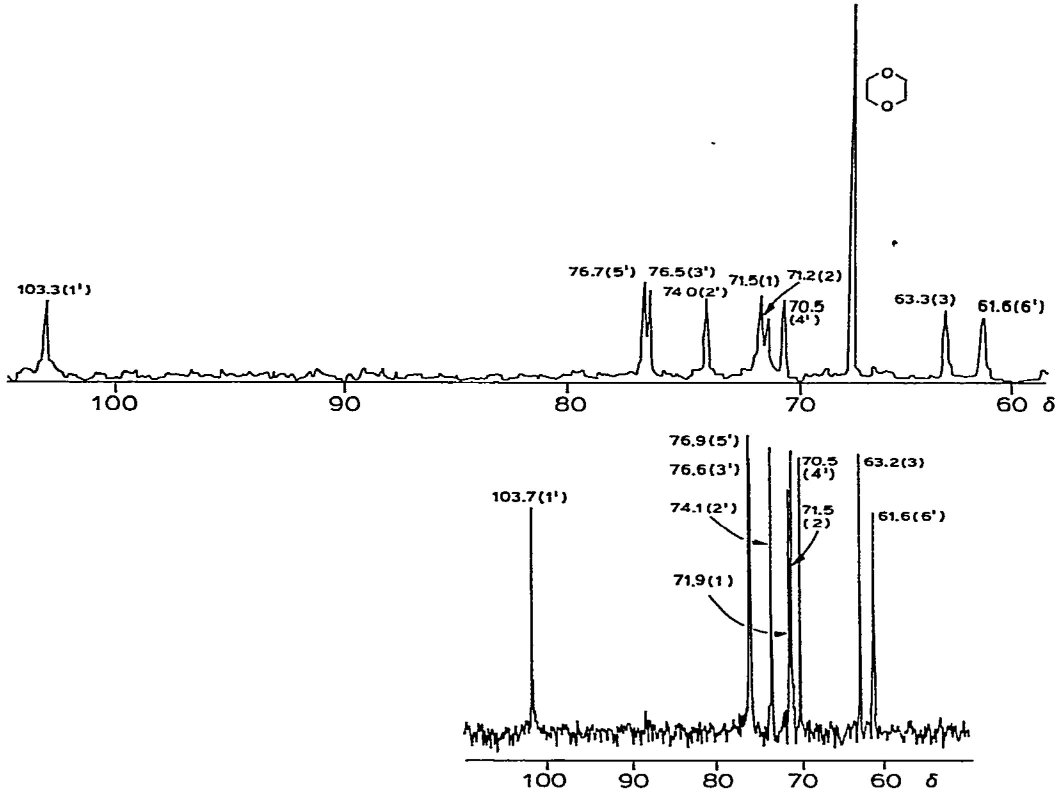


Fig. 3. ^{13}C-N.m.r. spectra of 1-*O*-β-D-glucopyranosyl-D-glycerol (above) and 1-*O*-β-D-glucopyranosyl-L-glycerol (below) in D_2O.

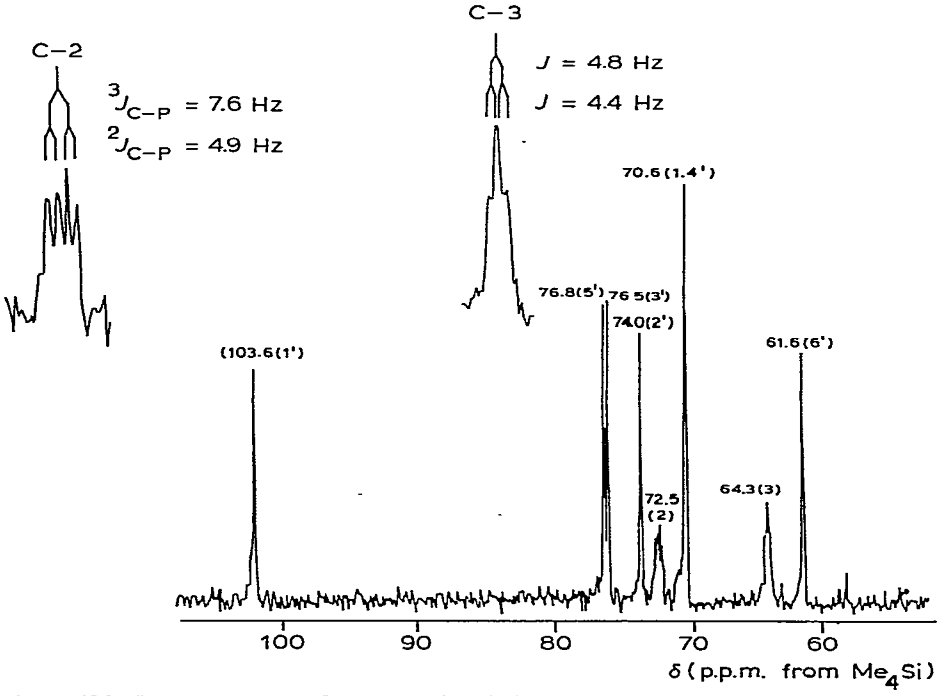
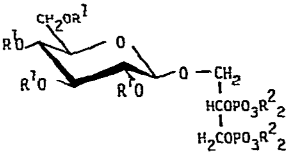
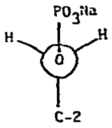


Fig. 4. ^{13}C-N.m.r. spectrum of compound **21** in D_2O.



20 R^1 = Ac, R^2 = Ph

21 R^1 = H, R^2 = Na



22

TABLE I

^3J AND ^2J VALUES (Hz) BETWEEN ^{13}C AND ^{31}P

Compound[a]	$^3J_{C-2,P}$	$^2J_{C-2,P}$	$^3J_{C-3,P}$	$^2J_{C-3,P}$
1	7.8			4.9
13	6.7			4.9
2	7.8			4.9
19	5.9			4.9
21	7.6	4.9	4.0	4.8

[a] Numbering of the carbon atoms of the glycerol is according to the D and L nomenclature.

Observed ^{13}C–^{31}P coupling-constants for the synthetic compounds **1**, **2**, **13**, **19**, and **21** are summarized in Table I. A large, three-bond coupling[8] of ~7 Hz between the ^{31}P atom of the phosphate group on the primary hydroxyl group and the ^{13}C-2 atom in all of the compounds revealed the *anti* orientation **22** between C-2 and the phosphate group.

EXPERIMENTAL

General. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were determined with a Perkin–Elmer Model 141 polarimeter for solutions in chloroform (analytical-reagent grade), unless otherwise noted. I.r. spectra were recorded with an EPI-G2 Hitachi spectrophotometer, as KBr discs for the crystalline samples and as neat films for the liquid samples. ^1H-N.m.r. spectra were recorded with a Varian HA-100 n.m.r. spectrometer, using tetramethylsilane as the internal standard. ^{13}C-N.m.r. spectra were recorded with a JNM-FX100FT n.m.r. spectrometer operated at 25.05 MHz. The values of δ_C and δ_H are expressed in p.p.m. downward from the internal standard. Column chromatography was performed on columns of Silica Gel Merck (70–230 mesh; E. Merck, Darmstadt, Germany). Thin-layer chromatography was performed on precoated plates (layer thickness, 0.25 mm; E. Merck, Darmstadt, Germany) of Silica Gel 60 F_{254}.

2,3-O-Isopropylidene-1-O-(tributyltin)-D-glycerol (**4**). — A mixture of 13.2 g (0.1 mol) of 1,2-*O*-isopropylidene-L-glycerol and 30 g (0.05 mol) of bis(tributyl)tin oxide in toluene (200 ml) was boiled under reflux during 8 h, with continuous removal of water. Evaporation of the toluene, and distillation of the residual oil, gave 26.1 g (62%) of **4**, b.p. 129–130°/0.14 mm Hg; $[\alpha]_D^{20}$ +13.7° (neat).

Anal. Calc. for $C_{18}H_{38}O_3Sn$: C, 51.33; H, 9.09. Found: C, 51.13; H, 8.94.

*3,4,6-Tri-O-acetyl-1,2-O[(2,3-O-isopropylidene-*D*-glycerol-1-yl)orthoacetyl]-α-*D*-glucopyranose* (**5**). — To a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (822 mg, 2 mmol) in dry 1,2-dichloroethane (20 ml) were added compound **4** (847 mg, 2 mmol) and tetraethylammonium bromide (100 mg, 0.48 mmol), and the mixture was stirred during 26 h at 55°. Evaporation of the solvent afforded an oil that was purified by chromatography on a column of silica gel (100 g). Elution with 80:20:1 benzene–ethyl acetate–triethylamine gave **5** (804 mg, 87%); crystals from di-isopropyl ether, m.p. 83–85°, $[\alpha]_D^{20}$ +32.1° (*c* 0.54); ^{1}H-n.m.r. data (chloroform-*d*): δ 1.34 and 1.40 (2 s, 3 H each, CMe_2), 1.72 (s, 3 H, orthoacetyl methyl), and 5.71 (d, 1 H, *J* 5 Hz, H-1').

Anal. Calc. for $C_{20}H_{30}O_{12}$: C, 51.94; H, 6.54. Found: C, 52.15; H, 6.45.

*2,3-O-Isopropylidene-1-O-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyl)-*D*-glycerol* (**6**). — A mixture of **5** (4 g, 18.7 mmol) and mercuric bromide (400 mg, 1.1 mmol) was stirred under nitrogen during 95 min at 135° (bath temperature). The mixture was then cooled to room temperature and submitted to chromatography on a column of silica gel (250 g). Elution with 2:1 benzene–ethyl acetate afforded 3.0 g (75%) of **6**; crystals from di-isopropyl ether, m.p. 109.5–111.5°, $[\alpha]_D^{20}$ —10.5° (*c* 0.51); ^{1}H-n.m.r. data (chloroform-*d*): δ 1.33 and 1.40 (2 s, 3 H each, CMe_2) and 4.61 (d, 1 H, *J* 7.5 Hz, H-1').

Anal. Calc. for $C_{20}H_{30}O_{12}$: C, 51.94; H, 6.54. Found: C, 52.02; H, 6.46.

*1-O-(2,3,4,6-Tetra-O-acetyl-β-*D*-glucopyranosyl)-*D*-glycerol*[7] (**7**). — Compound **6** (1.5 g, 3.25 mmol) in 20% aq. acetic acid (6 ml) was stirred during 70 min at 100° (bath temp.). Evaporation of the solvent gave an oil. A solution thereof in chloroform was successively washed with saturated sodium hydrogencarbonate solution and water, dried (anhydrous magnesium sulfate), and evaporated, to give a crystalline residue. Recrystallization from diethyl ether afforded 7, m.p. 105.5–109°, $[\alpha]_D^{20}$ —9.1° (*c* 0.52); ^{1}H-n.m.r. data (chloroform-*d*): δ 4.55 (d, 1 H, *J* 8.0 Hz, H-1').

*2-O-Acetyl-1-O-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyl)-3-O-trityl-*D*-glycerol* (**9**). — To 7 (300 mg, 0.71 mmol) in pyridine (2 ml) was added trityl chloride (238 mg, 0.85 mmol) at room temperature, and the mixture was stirred during 24 h at room temperature. Acetic anhydride (1 ml) was added, and the mixture was stirred for 15 h at room temperature, and then poured into ice–water. The mixture was extracted with ether, and the extract was washed successively with aq. potassium hydrogensulfate, aq. sodium hydrogencarbonate, and water, dried (anhydrous magnesium sulfate), and evaporated *in vacuo*. The residual oil was submitted to chromatography on a column of silica gel (30 g). Elution with 5:1 benzene–ethyl acetate afforded **9** (435 mg, 86.7%); crystals from di-isopropyl ether, m.p. 148–150°, $[\alpha]_D^{20}$ —28.9° (*c* 0.62); ^{1}H-n.m.r. data (chloroform-*d*): δ 4.50 (d, 1 H, *J* 8.0 Hz, H-1') and 7.2–7.5 (m, 15 H, Ph_3C).

Anal. Calc. for $C_{38}H_{42}O_{13}$: C, 64.58; H, 5.99. Found: C, 64.49; H, 5.92.

2-O-Acetyl-1-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-3-O-(diphenylphosphono)-D-glycerol (**11**). — Compound **9** (1 g, 1.41 mmol) in 80% aq. acetic acid (100 ml) was stirred during 1 h at 50° and evaporated *in vacuo*, with co-evaporation with toluene to remove acetic acid, giving a residual oil that was dissolved in pyridine (10 ml) and treated with diphenylphosphorochloridate (771 mg, 2.87 mmol). The mixture was stirred during 90 min at room temperature, poured onto ice–water, and extracted with ethyl acetate. The extract was successively washed with aq. sodium hydrogencarbonate and water, dried (anhydrous magnesium sulfate), and evaporated to an oil which was purified by chromatography on a column of silica gel (100 g). Elution with 2:1 benzene–ethyl acetate afforded **11** (717 mg, 72.7%) as an oil which was unstable at room temperature and had decomposed after 1 month; ^{1}H-n.m.r. data (chloroform-*d*): δ 7.10–7.44 (m, 10 H, aromatic H).

Anal. Calc. for $C_{31}H_{37}O_{16}P$: C, 53.45; H, 5.35. Found: C, 53.00; H, 5.45.

1-O-β-D-Glucopyranosyl-D-glycerol 3-(disodium phosphate) (**13**). — A solution of **11** (306 mg, 0.44 mmol) in ethyl acetate (10 ml) was stirred under hydrogen in the presence of platinum oxide (150 mg) during 2 h at room temperature. The catalyst was then filtered off, and the filtrate was evaporated *in vacuo*, giving an oil which was dissolved in 0.1M methanolic sodium methoxide (9 ml). The solution was stirred for 1 h at room temperature, and then concentrated *in vacuo* to ~4 ml. The concentrate was kept overnight at 5°, giving a white precipitate which was collected on a sintered-glass filter, washed with methanol, and dried *in vacuo*, to afford **13** as a hygroscopic solid (117 mg, 70.5%), m.p. 159–165°, $[\alpha]_D^{20}$ −17.3° (*c* 0.56, water); ^{1}H-n.m.r. data (D_2O): δ 4.46 (d, 1 H, *J* 8.0 Hz, H-1').

Anal. Calc. for $C_9H_{17}Na_2O_{11}P \cdot CH_3OH$: C, 29.27; H, 5.16. Found: C, 29.21; H, 5.41.

1-O-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-2-O-tosyl-3-O-trityl-D-glycerol (**14**). — To a solution of **7** (8.2 g, 19.4 mmol) in pyridine (70 ml) was added trityl chloride (6.5 g, 23.3 mmol), and the mixture was stirred during 38 h at room temperature. The pyridine was then removed by co-evaporation with toluene *in vacuo*. To the residue were added ethyl acetate and aq. sodium hydrogencarbonate; the ethyl acetate layer was washed with water, dried (anhydrous magnesium sulfate), and evaporated, giving an oil which was submitted to chromatography on a column of silica gel (340 g). Elution with 2:1 benzene–ethyl acetate afforded **8** (8.8 g, 68.2%). To a solution of **8** (4.0 g, 6.02 mmol) in pyridine (40 ml) was added *p*-toluenesulfonyl chloride (1.4 g, 7.34 mmol), and the mixture was stirred during 24 h at 70°, and cooled. Co-evaporation of the pyridine with toluene *in vacuo* gave an oil which was extracted with ethyl acetate. The extract was washed successively with aq. sodium hydrogencarbonate and water, dried (anhydrous magnesium sulfate), and evaporated, to give a crude product which was submitted to chromatography on a column of silica gel (200 g). Elution with 5:1 benzene–ethyl acetate afforded **14** (3.0 g, 76.5%); further elution, with 2:1 benzene–ethyl acetate, afforded **8** (0.81 g). Compound **14** was crystallized from diethyl ether, m.p. 164–166°, $[\alpha]_D^{20}$ −12.5° (*c* 0.55); ^{1}H-n.m.r. data (chloroform-*d*): δ 2.42 (s, 3 H, CH_3) and 4.46 (d, 1 H, *J* 8.0 Hz, H-1′).

Anal. Calc. for $C_{43}H_{46}O_{14}S$: C, 63.07; H, 5.66. Found: C, 63.08; H, 5.72.

*2-O-Acetyl-1-O-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyl)-3-O-trityl-*L*-glycerol* (**15**). — A solution of **14** (3.0 g, 3.7 mmol), potassium acetate (1.44 g, 14.7 mmol), and dibenzo-18-crown-6 (1.32 g, 3.67 mmol) in *N*,*N*-dimethylformamide (30 ml) was stirred during 3 days at 80°. The solution was then cooled and the *N*,*N*-dimethylformamide was evaporated *in vacuo*. The residue was extracted with ethyl acetate, and the extract was washed with water, dried (anhydrous magnesium sulfate), and evaporated, giving an oil which was submitted to chromatography on a column of silica gel (400 g). Elution with 5:1 benzene–ethyl acetate afforded **15** (1.55 g, 60%) as an oil; $[\alpha]_D^{20}$ −12.9° (*c* 0.51); ^{1}H-n.m.r. data (chloroform-*d*): δ 4.53 (d, 1 H, *J* 7.0 Hz, H-1′).

Anal. Calc. for $C_{38}H_{42}O_{13}$: C, 64.58; H, 5.99. Found: C, 63.88; H, 5.98.

*2-O-Acetyl-1-O-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyl)-3-O-(diphenylphosphono)-*L*-glycerol* (**17**). — Compound **15** (1.0 g, 1.42 mmol) in 80% aq. acetic acid (100 ml) was stirred during 90 min at 53°, and cooled. Co-evaporation of the acetic acid from the mixture with toluene *in vacuo* afforded a residue (**16**). To a solution of **16** in pyridine (10 ml) was added diphenylphosphorochloridate (784 mg, 2.92 mmol), and the mixture was stirred during 70 min at room temperature, and then poured into ice–water. The aqueous layer was extracted with ethyl acetate, and the extract was washed with water, dried (anhydrous magnesium sulfate), and evaporated, affording an oil which was submitted to chromatography on a column of silica gel (150 g). Elution with 2:1 benzene–ethyl acetate afforded **17** (439 mg, 45%); R_F 0.45 on a plate of silica gel (2:1 benzene–ethyl acetate); ^{1}H-n.m.r. data (chloroform-*d*): δ 1.98–2.01 (m, 15 H, 5 Me) and 7.06–7.46 (m, 10 H, aromatic H). As this oil is unstable at room temperature, it was used immediately for the next step.

*1-O-β-*D*-Glucopyranosyl-*L*-glycerol 3-(disodium phosphate)* (**19**). — A solution of **17** (439 mg, 0.63 mmol) in ethyl acetate (15 ml) was stirred under hydrogen in the presence of platinum oxide (200 mg) during 3.5 h at 40°. The catalyst was filtered off, and the filtrate was evaporated *in vacuo*, giving an oil (**18**) which was dissolved in 0.1M methanolic sodium methoxide (13 ml). The mixture was stirred during 2 h at room temperature, and concentrated to ~4 ml, and the concentrate was kept overnight at 5°. The resulting, white precipitate was collected on a sintered-glass filter, washed with cold methanol, and dried *in vacuo*; 118 mg (70%) of **19** was obtained as an amorphous material, m.p. 133–141° (dec.), $[\alpha]_D^{20}$ −28.9° (*c* 0.53, water).

Anal. Calc. for $C_9H_{17}Na_2O_{11}P \cdot CH_3OH$: C, 29.27; H, 5.16; Found: C, 29.47; H, 5.21.

*2,3-Di-O-(diphenylphosphono)-1-O-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyl)-*D*-glycerol* (**20**). — To a solution of diphenylphosphorochloridate (0.5 ml) in pyridine (1 ml) was added **7** (184 mg, 0.44 mmol) portionwise. The mixture was stirred during 2 h at room temperature, and then poured into ice–water. The aqueous phase was extracted with ethyl acetate, and the extract was combined with the organic layer, washed successively with aq. sodium hydrogencarbonate, and water, dried (anhydrous magnesium sulfate), and evaporated, affording an oil which was submitted to chromatography on a column of silica gel (30 g). Elution with 1:1 benzene–ethyl acetate afforded 73 mg (19%) of **20** as an oil; ^{1}H-n.m.r. data (chloroform-*d*): δ 1.96, 1.98, 2.01, and 2.03 (4 s, 3 H each, 4 acetyl Me). This oil was used immediately for the next step.

*1-O-β-*D*-Glucopyranosyl-*D*-glycerol 2,3-bis(sodium phosphate)* (**21**). — A solution of **20** (70 mg, 79 μmol) in ethyl acetate (3 ml) was stirred under hydrogen in the presence of platinum oxide (38 mg) during 2 h at room temperature. The catalyst was then filtered off and the filtrate was evaporated, affording an oil which was dissolved in 0.1M methanolic sodium methoxide (3.5 ml), and the mixture was stirred during 1 h at room temperature. Co-evaporation of the methanol with ethanol afforded **21** as an amorphous material which was washed with ethanol, and dried *in vacuo*; 27 mg, $[\alpha]_D^{20}$ $-14.8°$ (*c* 0.41, water).

ACKNOWLEDGMENTS

We thank Dr. H. Homma and his staff for the elemental analyses, and Dr. J. Uzawa and Mrs. T. Chijimatsu for recording and measuring the n.m.r. spectra.

REFERENCES

1 W. R. DeBoer, F. J. Kruyssen, J. T. M. Wouters, and C. Kruk, *Eur. J. Biochem.*, 62 (1976) 1–6.
2 B. Wickberg, *Acta Chem. Scand.*, 12 (1958) 1187–1201; H. P. Wehri and Y. Pomeranz, *Chem. Phys. Lipids*, 3 (1969) 357–370.
3 A. I. Bashkatova, V. N. Volynskaya, G. V. Smirnova, V. I. Shvets, and R. P. Evstigneeva, *J. Org. Chem. USSR*, 8 (1972) 548–552.
4 T. Ogawa and M. Matsui, *Carbohydr. Res.*, 51 (1976) c13–c18.
5 L. Lecocq and C. E. Ballou, *Biochemistry*, 3 (1964) 976–980.
6 R. U. Lemieux and A. R. Morgan, *Can. J. Chem.*, 43 (1965) 2199–2204.
7 A. I. Bashkatova, G. V. Smirnova, V. I. Shvets, and R. P. Evstigneeva, *J. Org. Chem. USSR*, 7 (1971) 1707–1714.
8 I. C. P. Smith, H. J. Jennings, and R. Deslauries, *Acc. Chem. Res.*, (1975) 306–313; D. R. Bundle, I. C. P. Smith, and H. J. Jennings, *J. Biol. Chem.*, 249 (1974) 2275–2281.