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SYNTHESIS OF PROPYL 4-*O*-(3,6-DI-*O*-METHYL-β-D-GLUCOPYRANOSYL)-2,3-DI-*O*-METHYL-α-D-RHAMNOPYRANOSIDE*

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ABSTRACT

Partial hydrolysis of allyl 2,3:4,6-di-*O*-isopropylidene-α-D-mannopyranoside gave allyl 2,3-*O*-isopropylidene-α-D-mannopyranoside which was converted into allyl 2,3-*O*-isopropylidene-α-D-rhamnopyranoside by reduction of the 6-*O*-tosyl derivative with lithium aluminium hydride. Condensation of allyl 2,3-*O*-isopropylidene-α-D-rhamnopyranoside with 2,4-di-*O*-acetyl-3,6-di-*O*-methyl-α-D-glucopyranosyl chloride in the presence of mercury(II) cyanide gave the crystalline β-linked disaccharide which was converted into the title compound.

INTRODUCTION

A unique phenolic glycolipid is produced by *Mycobacterium leprae*, grown in the nine-banded armadillo[2,3], and the oligosaccharide portion has the sequence[3,4] 3,6-di-*O*-methyl-β-glucose-(1→4)-2,3-di-*O*-methyl-α-rhamnose-(1→2)-3-*O*-methylrhamnose. Antibodies to the glycolipid are present in the sera of leprosy patients[3,5,6] and therefore the glycolipid and its oligosaccharide portion are of interest as diagnostic agents for leprosy infection at an early stage[7–10]. Monoclonal antibodies directed to the glycolipid have been produced[11] and the glycolipid has been shown to induce lymphocyte suppression[12].

We[1] and others[8] have synthesised the disaccharide unit 4-*O*-(3,6-di-*O*-methyl-β-D-glucopyranosyl)-2,3-di-*O*-methyl-L-rhamnopyranose and its propyl α-glycoside and shown[1,8,9] them to be serologically active in the ELISA test. In the structural studies reported[3,4] on the glycolipid, the absolute configurations of the sugar molecules were not determined and we have therefore prepared a glycoside of the corresponding disaccharide 4-*O*-(3,6-di-*O*-methyl-β-D-glucopyranosyl)-2,3-di-*O*-methyl-D-rhamnopyranose and compared its serological activity with that of the previously prepared disaccharide containing L-rhamnose.

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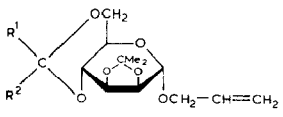
RESULTS AND DISCUSSION

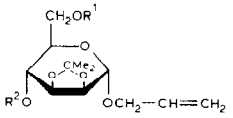
Protected derivatives of D-rhamnose have previously been obtained by the hydrogenolysis of 6-*O*-sulphonyl derivatives of D-mannose with lithium aluminium hydride[13,14], which is a good reagent for this purpose using ether as a solvent[15].

We required the allyl glycosides of the disaccharides, in order to allow the preparation of the free disaccharides and to provide a "handle" for coupling the product to a polymeric support, and therefore the required starting material was allyl α-D-mannopyranoside. This compound has been described by several workers[16–20] but few details have been recorded, although a melting point of 98–99° and a rotation of $[\alpha]_D^{25}$ +99° (water) were reported[16]. Recently, it was reported[19] that the Fischer glycosidation of mannose with allyl alcohol was best carried out under nitrogen in order to avoid oxidation of the reducing sugar, which diminishes the yield; a product with m.p. 138–139°, $[\alpha]_D$ +51.6° (water) was obtained.

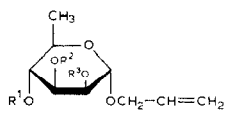
We found that very dark coloured products were obtained on treating mannose with refluxing allyl alcohol containing hydrogen chloride and that the glycoside is best prepared by stirring mannose with allyl alcohol, saturated with hydrogen chloride, at 20° for 20 h, although the product was not isolated crystalline. The crude allyl α-D-mannopyranoside was treated with dimethoxypropane and an acid catalyst to give the crystalline di-*O*-isopropylidene derivative **1**, which was readily partially hydrolysed to give the crystalline 2,3-*O*-isopropylidene derivative **4**, as described for the corresponding methyl glycoside[21]. Similar preparations of compounds **1** and **4** were reported by Kochetkov and his co-workers[20] after this work was completed, but we have recorded our procedures in detail since they have some preparative advantages.



1 $R^1 = R^2 =$ Me
2 $R^1 =$ Ph, $R^2 =$ H
3 $R^1 =$ Ph (*p*OMe), $R^2 =$ H



4 $R^1 = R^2 =$ H
5 $R^1 =$ H, $R^2 =$ Bzl
6 $R^1 =$ H, $R^2 = CH_2Ph$ (*p*OMe)
7 $R^1 =$ Tr, $R^2 =$ H
8 $R^1 =$ Tr, $R^2 =$ Bzl
9 $R^1 =$ Ms, $R^2 =$ Bzl
10 $R^1 =$ Ts, $R^2 =$ H

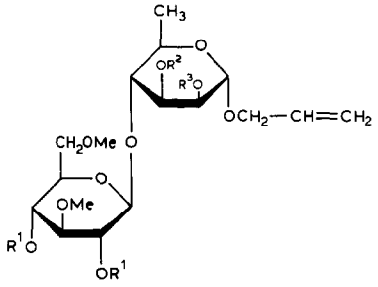


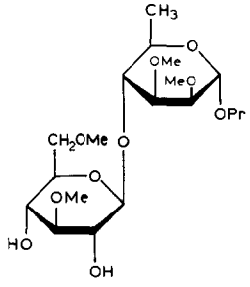
11 $R^1 =$ Bzl, $R^2, R^3 = >CMe_2$
12 $R^1 =$ H, $R^2, R^3 = >CMe_2$
13 $R^1 =$ Bzl, $R^2 = R^3 =$ H

Initially, it was intended to convert the isopropylidene derivative **4** into the 4-*O*-benzyl derivatives **5** and **6** by the action of sodium cyanoborohydride and trimethylsilyl chloride[22] or lithium aluminium hydride–aluminium chloride[23] on the corresponding benzylidene derivatives **2** and **3**; for this purpose, **2** and **3** were synthesised. The benzyl ether **5** was also synthesised by conversion of the diol **4** into the trityl ethers **7** and **8**, and subsequent hydrolysis of the trityl group in acidified acetone.

Subsequently, it was found that the best route to the required D-rhamnose derivatives **11** and **12** was *via* the tosylate **10**, which was prepared in high yield from the diol **4**. Reduction of **10** with lithium aluminium hydride in ether at 20° rapidly gave the D-rhamnose derivative **12**, which gave **11** on benzylation. Compound **11** was also prepared by reduction of the mesylate **9** with lithium aluminium hydride. Treatment of compound **9** with sodium borohydride in hot dimethyl sulphoxide[24] led to rapid deoxygenation at C-6 and also to saturation of the double bond of the allyl group, probably due to the formation of borane in the reaction mixture[25]. Compound **11** was hydrolysed to the crystalline diol **13**. The $[\alpha]_D$ values for **11**–**13** were opposite to those of their enantiomers[1], but otherwise their properties were identical.

Condensation of the alcohol **12** with 2,4-di-*O*-acetyl-3,6-di-*O*-methyl-α-D-glucopyranosyl chloride[1], under the conditions described previously[1] using the L-rhamnose derivative, gave the crystalline disaccharide **14**. ^{1}H-N.m.r. spectroscopy of the diol **15**, obtained from **14** by alkaline hydrolysis, confirmed the β linkage in the disaccharide. Compound **15** was converted, *via* compounds **16** and **17**, into the crystalline tetramethyl ether **18**, as described[1] for the disaccharide containing L-rhamnose. Hydrogenolysis of **18** gave the required disaccharide **19**, which showed similar activity[26] to the other disaccharide[9] in the ELISA test.





19

14 R^1 = Ac, R^2, R^3 = $>CMe_2$
15 R^1 = H, R^2, R^3 = $>CMe_2$
16 R^1 = Bzl, R^2, R^3 = $>CMe_2$
17 R^1 = Bzl, R^2, R^3 = H
18 R^1 = Bzl, R^2, R^2 = Me

EXPERIMENTAL

General methods. — Light petroleum had b.p. 40–60° and t.l.c. was carried out using silica gel G (Merck) unless otherwise stated. Solvents were evaporated under reduced pressure, and optical rotations were measured with a Bendix automatic polarimeter. ^{1}H-N.m.r. spectra (internal Me_4Si) were recorded with a Bruker WH-270 spectrometer.

*Allyl 2,3:4,6-di-*O*-isopropylidene-α-*D*-mannopyranoside*[20] (**1**). — A mixture

of D-mannose (10 g) and allyl alcohol saturated with hydrogen chloride (100 mL) was stirred at 20°. After 2 h, the resulting clear solution was kept at 20° for 20 h and then an excess of sodium hydrogencarbonate was added to the slightly coloured solution. The allyl alcohol was evaporated, and toluene was evaporated from the residue to remove the last traces of allyl alcohol. The residue was extracted with acetone (250 mL), the extract was filtered and concentrated to give the crude allyl α-D-mannopyranoside (12 g), and a solution of this product in acetone (150 mL) containing 2,2-dimethoxypropane (50 mL) and toluene-*p*-sulphonic acid monohydrate (1 g) was stored for 1 h at 20°. T.l.c. (ether–light petroleum, 1:1) then showed complete conversion of the starting material (R_F 0) into the product (R_F 0.85). An excess of triethylamine was added and the solvent was evaporated. Ether and saturated aqueous sodium hydrogencarbonate were added to the residue, and the ether extract was dried (K_2CO_3) and concentrated. The crude product (15.5 g) was eluted from a column of basic alumina (200 g) with ether–light petroleum (1:1) to give **1** (11.5 g, 69%) slightly contaminated with the presumed β isomer (R_F 0.7, as above). Recrystallisation from light petroleum (b.p. 60–80°) gave the pure product, m.p. 60–62°, $[\alpha]_D^{24}$ +13° (*c* 1, chloroform); lit.[20] m.p. 59°, $[\alpha]_D^{20}$ +12.5° (*c* 2, chloroform) (Found: C, 60.38; H, 8.12. Calc. for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05%).

*Allyl 2,3-*O*-isopropylidene-α-*D*-mannopyranoside*[20] (**4**). — Compound **1** (20.5 g) was added to a mixture of acetone (400 mL), water (10 mL), and toluene-*p*-sulphonic acid monohydrate (2 g) at 40°. After 15 min, triethylamine (4 mL) and sodium hydrogencarbonate (2.5 g) were added, and the solution was concentrated to near dryness. Water (20 mL) was added and the mixture was extracted with light petroleum to give **1** (4.5 g). Extraction of the aqueous layer with chloroform then gave **4** (13.3 g, 75%) which, after recrystallisation from ethyl acetate–light petroleum (b.p. 60–80°), had m.p. 80–81°, $[\alpha]_D^{26}$ +41° (*c* 1, chloroform); lit.[20] m.p. 76–78° $[\alpha]_D^{20}$ +37.5° (*c* 2, chloroform) (Found: C, 55.39; H, 7.96. Calc. for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75%).

*Allyl 4,6-*O*-benzylidene-2,3-*O*-isopropylidene-α-*D*-mannopyranoside* (**2**) *and allyl 2,3-*O*-isopropylidene-4,6-*O*-p-methoxybenzylidene-α-*D*-mannopyranoside* (**3**). — The diol **4** (1 g) was added to a solution of the appropriate benzaldehyde dimethyl acetal (1 g) and toluene-*p*-sulphonic acid monohydrate (50 mg) in acetonitrile (20 mL), and the solution was kept at 20° for 30 min. Triethylamine (0.5 mL) was then added and the solvent was evaporated. The crude product was eluted from a column of basic alumina with ether–light petroleum (1:1) to give **2**, m.p. 126–127° [from ethyl acetate–light petroleum (b.p. 60–80°)], $[\alpha]_D^{25}$ −4° (*c* 1, chloroform) (Found: C, 65.89; H, 7.01. Calc. for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94%); and **3**, m.p. 71–72.5°, $[\alpha]_D^{25}$ −5° (*c* 1, chloroform) (Found: C, 63.54; H, 6.74. Calc. for $C_{20}H_{26}O_7$: C, 63.48; H, 6.93%).

*Allyl 4-*O*-benzyl-2,3-*O*-isopropylidene-α-*D*-mannopyranoside* (**5**). — A solution of **4** (5 g) and chlorotriphenylmethane (6 g) in dry pyridine (50 mL) was kept at 50° for 5 h, and methanol (10 mL) was then added. After 30 min, sodium hydrogencarbonate (2 g) was added and the solvents were evaporated. Toluene

was evaporated from the residue to remove the last traces of pyridine. The crude product was extracted conventionally with ether and treated with an excess of benzyl bromide and sodium hydride in *N,N*-dimethylformamide at 20° until t.l.c. (ether–light petroleum, 1:2) showed complete conversion of the trityl derivative **7** (R_F 0.4) into the benzyl ether **8** (R_F 0.8). After addition of methanol and water, the crude product was extracted with ether, the extract was dried (K_2CO_3) and concentrated, and the crude product was treated with acetone (120 mL) and conc. hydrochloric acid (1 mL). After 45 min at 50°, t.l.c. (as above) showed complete hydrolysis of **8** to a major product (R_F 0.15). Excess of sodium hydrogencarbonate was added, the solvent was evaporated, and the crude product was subjected to chromatography on silica gel to give **5** (2 g, 30%), m.p. 74–75°, $[\alpha]_D^{25}$ +64° (*c* 1, chloroform) (Found: C, 65.23; H, 7.53. Calc. for $C_{19}H_{26}O_6$: C, 65.12; H, 7.48%).

*Allyl 2,3-*O*-isopropylidene-α-*D*-rhamnopyranoside* (**12**). — Toluene-*p*-sulphonyl chloride (11.8 g, 62 mmol) was added to a solution of **4** (12.3 g, 47 mmol) in dry pyridine (120 mL) at 0°. After 2 h, t.l.c. (ether–light petroleum, 2:1) showed complete conversion of **4** (R_F 0.25) into the tosyl derivative **10** (R_F 0.5). The solution was diluted with water and extracted with ether, and the extract was washed with ice-cold 3M hydrochloric acid, saturated aqueous potassium chloride, and saturated aqueous sodium hydrogencarbonate, dried ($MgSO_4$), and concentrated to give crude **10** (19.2 g). A solution of this product in dry ether (50 mL) was added dropwise to a stirred mixture of lithium aluminium hydride (2.5 g) in dry ether (100 mL) during 30 min. After a further 1 h, t.l.c. (ether–light petroleum, 2:1) showed complete conversion of **10** (R_F 0.5) into **12** (R_F 0.7). Ethyl acetate and water were then added, the inorganic material was removed, and the filtrate was dried (K_2CO_3) and concentrated. The crude product (10.1 g) was subjected to chromatography on basic alumina. After the elution of impurities with ether, **12** (8.25 g, 71%) was eluted with ether–methanol (49:1) as an oil, $[\alpha]_D^{26}$ +32° (*c* 1, chloroform); lit.[1] $[\alpha]_D^{24}$ −36.6° (*c* 1, chloroform) for the L isomer (Found: C, 59.30; H, 8.12. Calc. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.26%).

*Allyl 4-*O*-benzyl-α-*D*-rhamnopyranoside* (**13**). — (*a*) Methanesulphonyl chloride (1.5 mL, 19 mmol) was added slowly to a solution of **5** (4 g, 11 mmol) in dry pyridine (20 mL) at 0°. After 1 h, t.l.c. (toluene–acetone, 2:1) showed complete conversion of **5** (R_F 0.65) into the product (R_F 0.75). Ice–water was then added, the product was extracted with ether, and the extract was washed with ice-cold 3M hydrochloric acid, saturated aqueous potassium chloride, and saturated aqueous sodium hydrogencarbonate, and dried ($MgSO_4$). A solution of the resulting crude mesylate **9** in dry ether (10 mL) was added dropwise to a stirred mixture of lithium aluminium hydride (1.5 g) in dry ether (50 mL). After 2 h, t.l.c. (ether–light petroleum, 1:1) showed complete conversion of **9** (R_F 0.5) into the product (R_F 0.9) which was isolated as described for **12**. Column chromatography on basic alumina (ether–light petroleum, 1:2) gave the pure product as an oil (3.4 g, 89%) from which the isopropylidene group was hydrolysed, as described[1] for the L isomer, to give **13**, m.p. 69–70°, $[\alpha]_D^{25}$ +70° (*c* 1, chloroform); lit.[1] m.p. 68–70°,

$[\alpha]_D^{25}$ −71.5° (*c* 1, chloroform), for the L isomer (Found: C, 65.56; H, 7.32. Calc. for $C_{16}H_{22}O_5$: C, 65.28; H, 7.53%).

(*b*) Allyl 2,3-*O*-isopropylidene-α-D-rhamnopyranoside (**12**) was treated with an excess of benzyl bromide and sodium hydride in *N,N*-dimethylformamide, and the product was isolated in the usual way and hydrolysed as described in (*a*) to give material identical with that described above.

Allyl 4-O-(2,4-di-O-acetyl-3,6-di-O-methyl-β-D-glucopyranosyl)-2,3-O-isopropylidene-α-D-rhamnopyranoside (**14**). — A mixture of 2,4-di-*O*-acetyl-3,6-di-*O*-methyl-α-D-glucopyranosyl chloride[1] (3 g, 9.6 mmol), **12** (1.9 g, 7.8 mmol), mercury(II) cyanide (1.7 g, 6.7 mmol), and dry acetonitrile (20 mL) was heated under reflux for 1.25 h. T.l.c. (ether–light petroleum, 2:1) then showed conversion of **12** and the glycosyl chloride (both with R_F 0.7) into a major (R_F 0.4) and a minor product (R_F 0.6). The solution was cooled and concentrated to dryness, and ether and saturated aqueous potassium iodide were added to the residue. The ether extract was dried ($MgSO_4$) and concentrated, and the crude product was subjected to chromatography on silica gel. Elution with ether gave the major product (1.5 g, 37% from **12**), which was recrystallised from ethyl acetate–light petroleum (b.p. 60–80°) to give **14**, m.p. 112–114°, $[\alpha]_D^{23.5}$ +11° (*c* 1, chloroform) (Found: C, 55.65; H, 7.39. Calc. for $C_{24}H_{38}O_{12}$: C, 55.59; H, 7.39%).

Saponification of **14** with sodium hydroxide in methanol, as described[1] for the related compound containing L-rhamnose, gave **15** as an oil. ^{1}H-N.m.r. data: δ 5.0 (s, rhamnose H-1), 4.46 (d, $J_{1,2}$ 8.2 Hz, glucose H-1), 3.39, 3.67 (2 s, 2 OMe), 1.35, 1.55 (2 s, CMe_2), 1.32 (d, rhamnose H-6,6,6).

Allyl 4-O-(2,4-di-O-benzyl-3,6-di-O-methyl-β-D-glucopyranosyl)-2,3-O-isopropylidene-α-D-rhamnopyranoside (**16**). — The diol **15** was benzylated with benzyl bromide and sodium hydride in *N,N*-dimethylformamide, as described[1] for the corresponding compound containing L-rhamnose, to give **16** as an oil, $[\alpha]_D^{25}$ +19.5° (*c* 0.93, chloroform) (Found: C, 66.77; H, 7.62. Calc. for $C_{34}H_{46}O_{10}$: C, 66.43; H, 7.54%).

Allyl 4-O-(2,4-di-O-benzyl-3,6-di-O-methyl-β-D-glucopyranosyl)-α-D-rhamnopyranoside (**17**). — Compound **16** (1 g) was added to a hot mixture of methanol (18 mL) and 6M hydrochloric acid (0.3 mL), and the solution was heated under reflux for 30 min and then cooled. An excess of sodium hydrogencarbonate was added, the solvents were evaporated, ether and magnesium sulphate were added to the residue, and the product isolated from the ether extract was subjected to chromatography on silica gel. Elution with ether gave **17** (0.75 g, 80%) as an oil, $[\alpha]_D^{25}$ +53° (*c* 0.9, chloroform) (Found: C, 64.70; H, 7.00. Calc. for $C_{31}H_{42}O_{10}$: C, 64.79; H, 7.37%).

Allyl 4-O-(2,4-di-O-benzyl-3,6-di-O-methyl-β-D-glucopyranosyl)-2,3-di-O-methyl-α-D-rhamnopyranoside (**18**). — Compound **17** was methylated as described[1] for the corresponding compound containing L-rhamnose. Recrystallisation of the product from light petroleum gave **18**, m.p. 52–53°, $[\alpha]_D^{29.7}$ +49° (*c* 0.95, chloroform) (Found: C, 66.08; H, 7.44. Calc. for $C_{33}H_{46}O_{10}$: C, 65.76; H, 7.69%).

Propyl 4-O-(3,6-di-O-methyl-β-D-glucopyranosyl)-2,3-di-O-methyl-α-D-rhamnopyranoside (**19**). — Compound **18** was hydrogenolysed as described[1] for the corresponding compound containing L-rhamnose. Column chromatography (ethyl acetate) of the product on silica gel gave **19** as a syrup, $[\alpha]_D^{29.8}$ +23° (*c* 0.95, chloroform) (Found: C, 53.50; H, 8.62. Calc. for $C_{19}H_{36}O_{10}$: C, 53.76; H, 8.55%).

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