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SYNTHESIS OF METHYL 3-*O*-α-D-MANNOPYRANOSYL-α-D-TALOPYRANOSIDE AND METHYL 3-*O*-α-D-TALOPYRANOSYL-α-D-TALOPYRANOSIDE*

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ABSTRACT

Methyl 2-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**4**) and methyl 2-*O*-benzyl-3-*O*-α-D-mannopyranosyl-α-D-mannopyranoside (**6**) were prepared from a common intermediate, namely, methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-mannopyranoside. On treatment with *tert*-butylchlorodiphenylsilane, in *N,N*-dimethylformamide in the presence of imidazole, **4** and **6** afforded methyl 2-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**7**), and methyl 2-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**8**), respectively. Compound **8** was converted into its 2,3-*O*-isopropylidene derivative (**9**), and oxidation of **7** and **9** with pyridinium chlorochromate, and reduction of the resulting carbonyl intermediates gave methyl 2-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-talopyranoside and methyl 2-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(6-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-isopropylidene-α-D-talopyranosyl)-α-D-talopyranoside, respectively. Removal of the protecting groups furnished the title disaccharides.

INTRODUCTION

In a previous paper in this series, we described the synthesis of methyl 2-*O*-α-D-mannopyranosyl-α-D-talopyranoside and methyl 2-*O*-α-D-talopyranosyl-α-D-talopyranoside[2]. These two disaccharides, as well as a variety of other related oligosaccharides, were required in a program for the study of the substrate specificity of the enzyme UDP-GlcNAc:lysosomal enzyme *N*-acetyl-α-D-glucosaminephospho-

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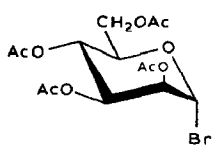
transferase (EC 2.4.8.17; "GlcNAc-*P*-transferase"). This enzyme is known to catalyze the transfer of a 2-acetamido-2-deoxy-α-D-glucopyranosyl phosphate group to selected D-mannose residues on lysosomal enzymes, in a process believed to be the initial step for the generation of the D-mannopyranosyl 6-phosphate-recognition marker of lysosomal enzymes, which appears to be involved in the targeting of newly synthesized lysosomal enzymes to lysosomes[3].

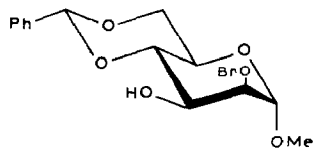
Thus, in a continuing effort to shed more light on the substrate-specificity of GlcNAc-*P*-transferase, we describe herein the synthesis of methyl 3-*O*-α-D-mannopyranosyl-α-D-talopyranoside, and methyl 3-*O*-α-D-talopyranosyl-α-D-talopyranoside. Our aim is, primarily, to study the change of the position of the interglycosidic linkage, and also that of the configuration at C-4 of the constituent sugar residues on the enzyme activity. It is also possible that such compounds may act as inhibitors for GlcNAc-*P*-transferase. Moreover, it could also be contemplated that such compounds may prove useful in the characterization of the α-D-mannosidases that are involved in the processing of *N*-glycosyl-linked glycoproteins[4].

RESULTS AND DISCUSSIONS

A common intermediate, namely, methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**3**), was employed for the synthesis of both of the title disaccharides.



1



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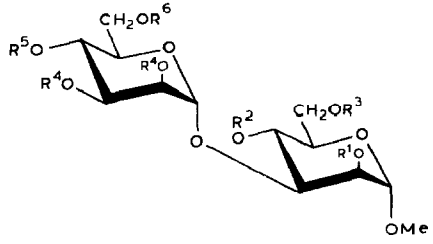
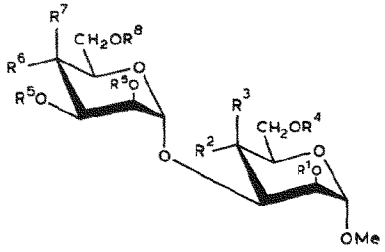


3 R^1 = Bn, R^2, R^3 = PhCH, R^4 = R^5 = R^6 = Ac
4 R^1 = Bn, R^2 = R^3 = H, R^4 = R^5 = R^6 = Ac
5 R^1 = Bn, R^2, R^3 = PhCH, R^4 = R^5 = R^6 = H
6 R^1 = Bn, R^2 = R^3 = R^4 = R^5 = R^6 = H
7 R^1 = Bn, R^2 = H, R^3 = Bu^tPh_2Si, R^4 = R^5 = R^6 = Ac
8 R^1 = Bn, R^2 = R^4 = R^5 = H, R^3 = R^6 = Bu^tPh_2Si
9 R^1 = Bn, R^2 = R^5 = H, R^4, R^4 = CMe_2, R^3 = R^6 = Bu^tPh_2Si

In one instance, the 4,6-*O*-benzylidene group of crude **3** (obtained by the condensation of **2** with bromide **1**) was cleaved in hot, 60% aqueous acetic acid to give, in 51% overall yield, the disaccharide methyl 2-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**4**). Alternatively, crude acetal **3** was *O*-deacetylated in methanolic sodium methoxide to afford, after column-chromatographic purification, methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-α-D-mannopyranosyl-α-D-mannopyranoside (**5**), the acetal group of which was, also, cleaved in hot 60% aqueous acetic acid to furnish the desired disaccharide intermediate (**6**). Treatment of **4** and **6** with *tert*-butylchlorodiphenylsilane in *N,N*-dimethylformamide, in the presence of imidazole, afforded the mono- and di-silylated derivatives **7** and **8**, respectively.



10 R^1 = Bn, R^2 = R^7 = H, R^3 = OH, R^4 = Bu^tPh_2Si, R^5 = R^8 = Ac, R^6 = OAc
11 R^1 = Bn, R^2 = R^5 = R^7 = R^8 = H, R^3 = R^6 = OH, R^4 = Bu^tPh_2Si
12 R^1 = Bn, R^2 = R^4 = R^5 = R^7 = R^8 = H, R^3 = R^6 = OH
13 R^1 = R^2 = R^4 = R^5 = R^7 = R^8 = H, R^3 = R^6 = OH
14 R^1 = Bn, R^2 = R^6 = H, R^3 = R^7 = OH, R^5, R^5 = CMe_2, R^4 = R^8 = Bu^tPh_2Si
15 R^1 = Bn, R^2 = R^4 = R^6 = R^8 = H, R^3 = R^7 = OH, R^5, R^5 = CMe_2
16 R^1 = Bn, R^2 = R^4 = R^5 = R^6 = R^8 = H, R^3 = R^7 = OH
17 R^1 = R^2 = R^4 = R^5 = R^6 = R^8 = H, R^3 = R^7 = OH

Oxidation of **7** with pyridinium chlorochromate in dichloromethane, in the presence of molecular sieves 3A, followed by reduction of the carbonyl group of the resulting intermediate with sodium borohydride in 95% aqueous ethanol, and subsequent *O*-deacetylation of the product mixture (containing tetraacetate **10**) in methanolic sodium methoxide afforded, in 80% overall yield, methyl 2-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-α-D-mannopyranosyl-α-D-talopyranoside (**11**). The tetra-acetate **10** could also be isolated by column chromatography, though in a substantially decreased yield (40%), because of concomitant *O*-deacetylation during sodium borohydride treatment.

Removal of the *tert*-butyldiphenylsilyl group of **11** by stirring with a molar solution of tetrabutylammonium fluoride in oxolan gave **12**, which was subjected to hydrogenolysis in the presence of 10% palladium-on-carbon to furnish methyl 3-*O*-α-D-mannopyranosyl-α-D-talopyranoside (**13**) as the hemihydrate, the ^{13}C-n.m.r. spectrum of which was consistent with the structure assigned (see Table I).

TABLE I

PROPOSED ^{13}C-N.M.R. CHEMICAL SHIFTS (δ) FOR DISACCHARIDES **13** AND **17**[a]

Chemical shift	*Compound*			
	α-D-*Man*p*OMe*[b]	α-D-*Talp*OMe[b]	**13**	**17**
C-1	101.9	102.2	98.57	99.39
C-2	71.2	70.7	70.34	70.39
C-3	71.8	66.2	71.38	71.34
C-4	68.0	70.3	67.31	67.43
C-5	73.7	72.1	72.32	72.34
C-6	62.1	62.3	62.49	62.50
C-1′			102.24	102.25
C-2′			71.08	71.13
C-3′			70.94	66.22
C-4′			67.71	70.54
C-5′			74.26	73.10
C-6′			61.90	62.50
OMe	55.9	55.6	55.81	55.85

[a]For solution in D_2O with Me_4Si as the external standard. [b]Ref. 7.

Acetalation of compound **8** with 2,2-dimethoxypropane in acetone, in the presence of *p*-toluenesulfonic acid, gave the 2,3-di-*O*-isopropylidene derivative **9**. When **9** was oxidized with pyridinium chlorochromate, and the resulting intermediate reduced with sodium borohydride in aqueous ethanol, it furnished, in 82% yield, the methyl α-D-talopyranosyl-α-D-talopyranoside derivative **14**. Removal of the protecting groups of **14** afforded the desired disaccharide **17**, by way of intermediates **15** and **16**, respectively. The ^{13}C-n.m.r. spectrum of **17** was, also, in accord with the structure assigned (see Table I).

EXPERIMENTAL

General methods. — The same methods were used as those already described[2], except for the following chromatographic solvent systems (v/v): (*A*) 9:1 chloroform–acetone, (*B*) 6:1 chloroform–methanol, (*C*) 9:1 chloroform–methanol, (*D*) 3:2 chloroform–hexane, and (*E*) 13:6:1 chloroform–methanol–water.

Methyl 2-O-benzyl-3-O-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**4**). — A stirred mixture of methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside[5] (**2**; 5 g), $Hg(CN)_2$ (4.5 g), and molecular sieves 4A (0.6 g) in nitromethane (25 mL) was boiled for 3 h, with azeotropic distillation, 12 mL of the solvent being finally removed. The mixture was cooled (~40–45°) and a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide[6] (**1**; 7.1 g) in nitromethane (25 mL) was added, and the stirring continued for 3 h at 40–45°. It was then cooled, diluted with benzene, and filtered. The filtrate was successively washed with saturated aqueous $NaHCO_3$, saturated aqueous KI solution, and

water, dried, and evaporated to a syrup. Examination by t.l.c. [4:1 (v/v) benzene–acetone] showed the disappearance of **2** and the presence of a major product, marginally slower-migrating than **2**. Several slower-migrating, minor contaminants (presumably resulting from the decomposition of **1**) were also revealed in t.l.c.

The crude product mixture (~8 g; containing **3**) was taken up in 60% aqueous acetic acid (300 mL) and heated for 2 h at 70°. The acetic acid was evaporated under diminished pressure, the last traces being removed by co-evaporation with several added portions of toluene. The residue was then applied to a column of silica gel and eluted with solvent *A*. On evaporation, fractions corresponding to the product afforded **4** (4.2, 51%) as an amorphous white solid, $[\alpha]_D^{23}$ +50.5° (*c* 0.9, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.90–21.9 (cluster of s, 12 H, OAc), 3.30 (s, 3 H, OMe), and 7.19–7.42 (m, 5 H, arom.).

Anal. Calc. for $C_{28}H_{38}O_{15}\cdot 0.5\ H_2O$: C, 53.93; H, 6.26. Found: C, 53.72; H, 6.26.

*Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-α-*D*-mannopyranosyl-α-*D*-mannopyranoside* (**5**). — To a solution of crude **3** (obtained as described above from 8 g of **2**), in methanol (100 mL) was added M methanolic sodium methoxide (10 mL), and the mixture stirred for 4 h at room temperature. The base was neutralized by the dropwise addition of glacial acetic acid, the solution evaporated to dryness, and the residue applied to a column of silica gel. Elution with solvent *C* yielded amorphous **5** (7 g, 60%), $[\alpha]_D^{23}$ +47° (*c* 1.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 3.21 (s, 3 H, OMe), 5.46 (s, 1 H, PhCH), and 7.05–7.35 (m, 10 H, arom.).

Anal. Calc. for $C_{27}H_{34}O_{11}\cdot H_2O$: C, 58.69; H, 6.52. Found: C, 59.07; H, 6.25.

*Methyl 2-*O*-benzyl-3-*O*-α-*D*-mannopyranosyl-α-*D*-mannopyranoside* (**6**). — Compound **5** (6.5 g) was taken up in 60% aqueous acetic acid (100 mL) and heated for 2 h at ~90°. Acetic acid was evaporated under reduced pressure, and several portions of toluene were added to, and evaporated from the residue, which was then purified in a column of silica gel with 4:1 (v/v) chloroform–methanol as the eluent to give **6** (5 g, 92%), a white powder, $[\alpha]_D^{23}$ +67.5° (*c* 0.9, methanol).

Anal. Calc. for $C_{20}H_{30}O_{11}\cdot 0.5\ H_2O$: C, 52.74; H, 6.81. Found: C, 52.73; H, 6.77.

*Methyl 2-*O*-benzyl-6-*O*-tert-butyldiphenylsilyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**7**). — To a cold (0°, bath) and stirred solution of **4** (4 g, 6.5 mmol) and imidazole (1.1 g, 16.1 mmol) in dry *N,N*-dimethylformamide (65 mL) was added *tert*-butylchlorodiphenylsilane (2 mL, 7.7 mmol), and the stirring was continued for 1 h at ~0°. After processing in the usual manner[2], the crude product was subjected to column-chromatography on silica gel with solvent *D* as the eluent to give **7** (4 g, 72%), amorphous, $[\alpha]_D^{23}$ +35.5° (*c* 1.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.06 (s, 9 H, CMe_3), 1.90–2.15 (cluster of s, 12 H, OAc), 3.25 (s, 3 H, OMe), and 7.18–7.96 (m, 15 H, Arom.).

Anal. Calc. for $C_{44}H_{56}O_{15}Si$: C, 61.97; H, 6.57. Found: C, 61.81; H, 6.84.

*Methyl 2-*O*-benzyl-6-*O*-tert-butyldiphenylsilyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-mannopyranosyl)-α-*D*-talopyranoside* (**10**) *and methyl 2-*O*-benzyl-6-*O*-tert-butyl-*

diphenylsilyl-3-O-α-D-mannopyranosyl-α-D-talopyranoside (**11**). — A mixture of **7** (2 g), molecular sieves 3A (4.9 g), and pyridinium chlorochromate (2.7 g) in dichloromethane (80 mL) was stirred for 12 h at room temperature. The mixture was diluted with ether (140 mL) and passed through a short column of silica gel. The eluate was concentrated to a syrup which was dissolved in 95% ethanol (20 mL), cooled (0°), treated with $NaBH_4$ (0.7 g), and stirred for 1 h at 0°. After neutralization with aqueous acetic acid, the solution was evaporated to dryness, and the residue dissolved in chloroform. The chloroform solution was repeatedly washed with water, till neutral, dried, and evaporated. T.l.c. (solvent *A*) showed the presence of a major product, accompanied by several slower-migrating contaminants (presumably due to *O*-deacetylation). The crude mixture (containing **10**; see later) was dissolved in methanol (50 mL), treated with M methanolic sodium methoxide (5 mL), and stirred for 4 h at room temperature. The base was neutralized by the addition of a few drops of glacial acetic acid, methanol and acetic acid were removed under reduced pressure, and the residue was applied to a column of silica gel. On elution with solvent *C*, evaporation of the fractions corresponding to the product gave **11** (0.8 g, 80%), white powder, $[\alpha]_D^{23}$ +55.5° (*c* 0.8, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.03 (s, 9 H, CMe_3), 3.22 (s, 3 H, OMe), and 7.16–7.82 (m, 15 H, arom.).

Anal. Calc. for $C_{36}H_{48}O_{11}Si$: C, 63.16; H, 7.02. Found: C, 63.17; H, 7.14.

In another experiment, **7** (1.1 g) was oxidized with pyridinium chlorochromate and then reduced with $NaBH_4$ as aforedescribed. The crude product was subjected to column chromatography on silica gel with solvent *D* as the eluent to give **10** (0.4 g, 40%), white amorphous solid, $[\alpha]_D^{23}$ +60° (*c* 1.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.04 (s, 9 H, CMe_3), 1.82–2.25 (cluster of s, 12 H, OAc), 3.24 (s, 3 H, OMe), and 7.08–7.74 (m, 15 H, arom.).

Anal. Calc. for $C_{44}H_{56}O_{15}Si$: C, 61.97; H, 6.57. Found: C, 62.06; H, 6.62.

Methyl 2-O-benzyl-3-O-α-D-mannopyranosyl-α-D-talopyranoside (**12**). — A solution of **11** (0.7 g) in dry oxolan (20 mL) was stirred for 3 h at room temperature in the presence of M tetrabutylammonium fluoride (1.2 mL) in oxolan. The mixture was concentrated to dryness, and the residue purified in a column of silica gel with solvent *B* as the eluent to afford **12** (0.33 g, 72%), amorphous, $[\alpha]_D^{23}$ +88.5° (*c* 0.9, methanol).

Anal. Calc. for $C_{20}H_{30}O_{11}$: C, 53.81; H, 6.72. Found: C, 53.57; H, 6.57.

Methyl 3-O-α-D-mannopyranosyl-α-D-talopyranoside (**13**). — A mixture of **12** (0.25 g) and 10% Pd–C (0.1 g) in 3:1 ethanol–glacial acetic acid (10 mL) was shaken under H_2 at ~345 kPa for 16 h at room temperature. The suspension was filtered (Celite), the solids were thoroughly washed with methanol, and the filtrate and washings combined and evaporated. The residue was purified in a column of silica gel with solvent *E* as the eluent to afford **13** (0.18 g, 95%) amorphous. $[\alpha]_D^{23}$ +133° (*c* 0.9, methanol); for ^{13}C-n.m.r. data, see Table I.

Anal. Calc. for $C_{13}H_{24}O_{11} \cdot 0.5\ H_2O$: C, 42.72; H, 6.85. Found: C, 43.00; H, 6.93.

Methyl 2-O-benzyl-6-O-tert-butyldiphenylsilyl-3-O-(6-O-tert-butyldiphenylsilyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**8**). — To a cold (0°) and stirred solution of **6** (4.8 g, 10.6 mmol), in dry *N,N*-dimethylformamide (45 mL) containing imidazole (3.5 g, 51.1 mmol), was added *tert*-butylchlorodiphenylsilane (6.5 g, 24.6 mmol), and the stirring was continued for 1 h at 0°. After processing as described for **4** (to give **7**), followed by column chromatographic purification on silica gel with solvent *B* as the eluent, **8** (7.3 g, 74.4%) was obtained as a white amorphous solid, $[\alpha]_D^{23}$ +16.8° (*c* 0.9, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.19 (s, 18 H, CMe_3), 3.20 (s, 3 H, OMe), and 7.20–7.75 (m, 25 H, arom.).

Anal. Calc. for $C_{52}H_{66}O_{11}Si_2$: C, 67.68; H, 7.16. Found: C, 67.48; H, 7.29.

Methyl 2-O-benzyl-6-O-tert-butyldiphenylsilyl-3-O-(6-O-tert-butyldiphenylsilyl-2,3-O-isopropylidene-α-D-mannopyranosyl)-α-D-mannopyranoside (**9**). — To a solution of **8** (6.9 g) in dry acetone (80 mL) were added 2,2-dimethoxypropane (80 mL) and *p*-toluenesulfonic acid monohydrate (0.9 g). The mixture was stirred for 1 h at room temperature, made neutral by the addition of triethylamine, and then evaporated. The residue was dissolved in chloroform, the chloroform solution washed with water, dried, and evaporated to dryness. The residue was purified in a column of silica gel with 9:1 (v/v) toluene–ethyl acetate as the eluent to give **9** (6.1 g, 84.3%), a white solid, $[\alpha]_D^{23}$ +4.8° (*c* 1.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.05 (s, 18 H, CMe_3), 1.32 and 1.46 (s, 3 H each, CMe_2), 3.20 (s, 3 H, OMe), and 7.09–7.74 (m, 25 H, arom.).

Anal. Calc. for $C_{55}H_{70}O_{11}Si_2$: C, 68.61; H, 7.28. Found: C, 68.76; H, 7.26.

Methyl 2-O-benzyl-6-O-tert-butyldiphenylsilyl-3-O-(6-O-tert-butyldiphenylsilyl-2,3-O-isopropylidene-α-D-talopyranosyl)-α-D-talopyranoside (**14**). — A stirred solution of **9** (6 g) in dichloromethane (200 mL) containing powdered molecular sieves 3A (18 g) was treated with pyridinium chlorochromate (21.9 g), and the stirring was continued for 24 h at room temperature. The mixture was diluted with ether (200 mL) and passed through a short column of silica gel. The eluate was evaporated to dryness under reduced pressure to give a syrup, ν_{max}^{film} 1740 (C=O), which was directly reduced with $NaBH_4$ (4.1 g) in aqueous ethanol in a manner analogous to that described above for the synthesis of **11**. The crude mixture was then subjected to column chromatography on silica gel with 9:1 (v/v) chloroform–hexane as the eluent to afford **14** (4 g, 81.6%), amorphous, $[\alpha]_D^{23}$ +25.4° (*c* 1.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.06 (s, 18 H, CMe_3), 1.41 and 1.54 (s, 3 H each, CMe_2), 3.20 (s, 3 H, OMe), and 7.20–7.80 (m, 25 H, aromatic).

Anal. Calc. for $C_{55}H_{70}O_{11}Si_2$: C, 68.61; H, 7.28. Found: C, 68.59; H, 7.39.

Methyl 2-O-benzyl-3-O-(2,3-O-isopropylidene-α-D-talopyranosyl)-α-D-talopyranoside (**15**). — A solution of **14** (3.5 g) in dry oxolan (70 mL) was treated with a molar solution of tetrabutylammonium fluoride in oxolan (7.7 mL) as described for **11** (to give **12**). The mixture was purified on a column of silica gel with 12:1 (v/v) chloroform–methanol as the eluent to afford amorphous **15** (1.6 g, 94%), $[\alpha]_D^{23}$ +60° (*c* 0.7, chloroform); ^{1}H-n.m.r. ($CDCl_3$): 1.40 and 1.57 (s, 3 H each, CMe_2), 3.35 (s, 3 H, OMe), and 7.26 (m, 5 H, arom.).

Anal. Calc. for $C_{23}H_{34}O_{11} \cdot H_2O$: C, 54.76; H, 7.14. Found: C, 54.93; H, 7.18.

Methyl 2-O-benzyl-3-O-α-D-talopyranosyl-α-D-talopyranoside (**16**). — Compound **15** (1.6 g) in 60% aqueous acetic acid (50 mL) was heated for 1 h at 60°. Acetic acid was evaporated under diminished pressure, the last traces being removed by co-evaporation with several added portions of toluene. The residue was purified in a column of silica gel by use of solvent *B* as the eluent to give **16** (1.2 g, 86%), $[\alpha]_D^{23}$ +89° (*c* 1.0, methanol).

Anal. Calc. for $C_{20}H_{30}O_{11} \cdot 0.5\ H_2O$: C, 52.73; H, 6.87. Found: C, 52.64; H, 6.84.

Methyl 3-O-α-D-talopyranosyl-α-D-talopyranoside (**17**). — Hydrogenolysis of **16** (1 g) in 3:1 ethanol–acetic acid (20 mL) in the presence of Pd–C (0.3 g) as described for **12** (to give **13**), gave, after column-chromatographic purification with solvent *E* as the eluent, **17** (0.66 g, 83%), $[\alpha]_D^{23}$ 144° (*c* 1.0, methanol); for ^{13}C-n.m.r. data, see Table I.

Anal. Calc. for $C_{13}H_{24}O_{11} \cdot H_2O$: C, 41.71; H, 6.95. Found: C, 41.76; H, 6.86.

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