Carbohydrate Research, 84 (1980) 211–224
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

PRACTICAL SYNTHESIS OF *O*-β-D-MANNOPYRANOSYL-, *O*-α-D-MANNOPYRANOSYL-, AND *O*-β-D-GLUCOPYRANOSYL-(1→4)-*O*-α-L-RHAMNOPYRANOSYL-(1→3)-D-GALACTOSES

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(Received September 24th, 1979; accepted for publication, November 28th, 1979)

ABSTRACT

The Koenigs–Knorr glycosylation of 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-3-*O*-(2,3-*O*-isopropylidene-α-L-rhamnopyranosyl)-α-D-galactopyranose (**3**) by 4,6-di-*O*-acetyl-2,3-*O*-carbonyl-α-D-mannopyranosyl bromide (**10**), as well as Helferich glycosylations of **3** by tetra-*O*-acetyl-α-D-mannopyranosyl and -α-D-glucopyranosyl bromides, proceeded smoothly to give high yields of trisaccharide derivatives (**12**, **16**, and **17**). An efficient procedure for the transformation of **12**, **16**, and **17** into the α-deca-acetates of the respective trisaccharides has been developed. Zemplén deacetylation then afforded the title trisaccharides in yields of 53, 52, and 62%, respectively, from **3**. A new route to 1,4,6-tri-*O*-acetyl-2,3-*O*-carbonyl-α-D-mannopyranose is suggested.

INTRODUCTION

Chemical syntheses of *O*-β-D-mannopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→3)-D-galactose, which represents the repeating unit of the *Salmonella newington* O-specific polysaccharide, and of its α-D-*manno* and β-D-*gluco* analogues, have been reported from our laboratory[1–8]. These syntheses were based on glycosylation of partially protected D-galactose derivatives by peracetylated hexosylrhamnosyl bromides.

Glycosylation of benzyl 2,6-di-*O*-acetyl-β-D-galactopyranoside gave moderate yields of isomeric trisaccharides having 3-*O*- and 4-*O*-substituted galactose residues[1–3]. 1,2:5,6-Di-*O*-isopropylidene-α-D-galactofuranose could be glycosylated more effectively[4–6], but removal of the protecting groups caused difficulties[4,6]. The best results by this approach were obtained with 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-α-D-galactopyranose (**1**) as the aglycon component[7,8].

We now report a new method for the practical synthesis of the title trisaccharides and the respective α-deca-acetates, based on successive attachment of monosaccharide units starting from the reducing terminus.

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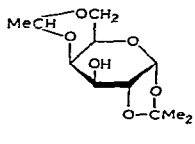
RESULTS AND DISCUSSION

The key disaccharide derivative in the present reaction scheme, 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-3-*O*-(2,3-*O*-isopropylidene-α-L-rhamnopyranosyl)-α-D-galactopyranose (**3**), was synthesised as follows. Condensation of tri-*O*-acetyl-α-L-rhamnopyranosyl bromide with crystalline **1** in acetonitrile in the presence of mercuric cyanide, followed by column chromatography, afforded 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-D-galactopyranose (**2**) in 92% yield. The structure of **2** was established by analytical and spectral data as well as by its conversion into the known[9] 3-*O*-α-L-rhamnopyranosyl-D-galactose (**6**) in 88% yield.



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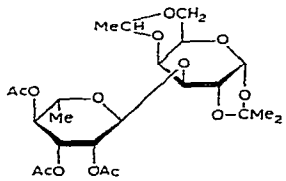

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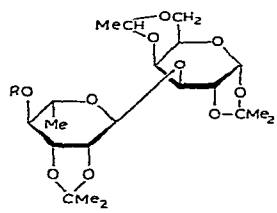

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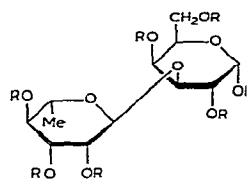
4 R = Ac



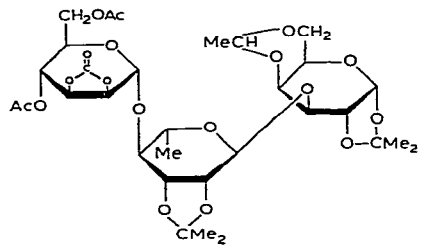
5 R = Ac
6 R = H

The protected disaccharide **2** was subjected to deacetylation and, without isolation, the product was treated with acetone–2,2-dimethoxypropane in the presence of anhydrous copper sulphate and *p*-toluenesulphonic acid at room temperature, to give, after column chromatography, 88% of **3**. The structures of **3** and of its crystalline acetate **4** were confirmed by analytical and spectral data. Moreover, **4** could be converted into **6** and quantitatively deacetylated to regenerate **3**.

Several successful syntheses of β-D-mannopyranosides[10,11] demonstrated that 4,6-di-*O*-acetyl-2,3-*O*-carbonyl-α-D-mannopyranosyl bromide (**10**) is an effective glycosylating agent. Compound **10** can be prepared by conventional treatment of 1,4,6-tri-*O*-acetyl-2,3-*O*-carbonyl-D-mannopyranose of any anomeric composition. We have developed an improved procedure for synthesis of crystalline 1,4,6-tri-*O*-acetyl-2,3-*O*-carbonyl-α-D-mannopyranose (**9**) from methyl α-D-mannopyranoside in 48% overall yield. Thus, treatment of methyl α-D-mannopyranoside with methyl isopropenyl ether[12] gave methyl 4,6-*O*-isopropylidene-α-D-mannopyranoside (**7**) in 91% yield. Treatment of **7** with 3 molar equivalents of methyl chloroformate, under conditions used for carbonylation of methyl 4,6-*O*-benzylidene-α-D-mannopyranoside[11], afforded the crystalline 2,3-carbonate **8** in 74% yield. Hydrolysis of **8** with 90% trifluoroacetic acid[13] followed by acetolysis gave the known[11], crystalline α-acetate **9** in 71% yield. The syrupy mother-liquor consisted of **9** and its β anomer and could also be used for synthesis of **10**. This reaction sequence gave a two-fold increase in the yield of crystalline **9**, which was accessible hitherto by a rather laborious route[11].

Although methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside can be readily

glycosylated[11] by bromide **10**, only traces of the expected trisaccharide derivative were obtained on attempted glycosylation of disaccharide **3** with **10** under essentially the same reaction conditions (dichloromethane, silver oxide, and molecular sieve). This result may be connected with considerable steric hindrance to glycosylation of the disaccharide derivative **3** by the silver oxide-absorbed[14] mannosyl bromide **10**, in comparison to that of methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside. Addition of a catalytic amount of silver perchlorate accelerated the reaction markedly and gave an 82% yield of a mixture of anomeric trisaccharide derivatives **11** and **12** in the ratio 12:88. From this mixture, pure **12** was isolated in 66% yield. The structures of **11** and **12** were established from analytical and spectral data as well as by their conversion into the known compounds **14**, **15**, and **19**. Decarbonylation of **11** and **12** followed by acetylation gave **16** and **13**, respectively.



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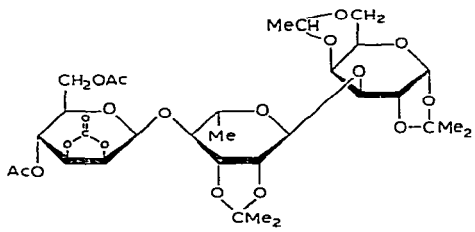

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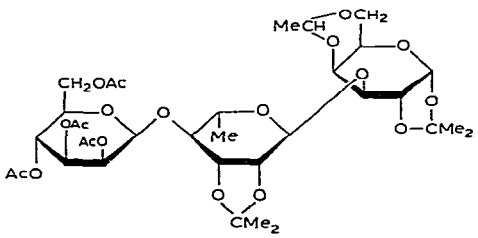

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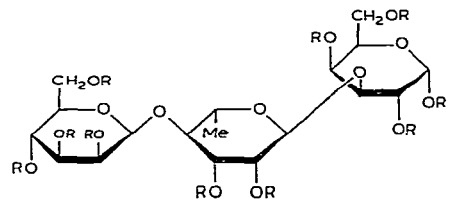
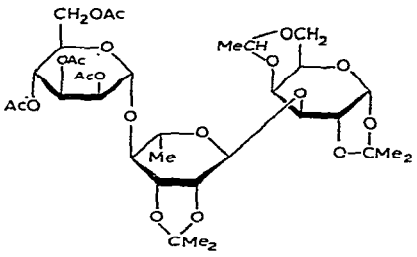


14 R = Ac
15 R = H

Glycosylation of **3** by tetra-*O*-acetyl-α-D-mannopyranosyl and -α-D-glucopyranosyl bromides in acetonitrile in the presence of mercuric cyanide proceeded smoothly, to give the corresponding trisaccharide derivatives **16** and **17** in yields of 72 and 81%, respectively, calculated from **3**. Analytical and spectral data of **16** and **17**, as well as their conversion into the known compounds **19**, **20**, and **21**, confirmed their structures.

Another set of trisaccharide derivatives (**23**, **25**, and **27**) was obtained by using the scheme described[7,8] for the synthesis of **23** and **25**, namely, glycosylation of **1** by the appropriate hexosylrhamnosyl bromide (**22**, **24**, and **26**). These condensations, performed in acetonitrile in the presence of mercuric cyanide, afforded (after chro-



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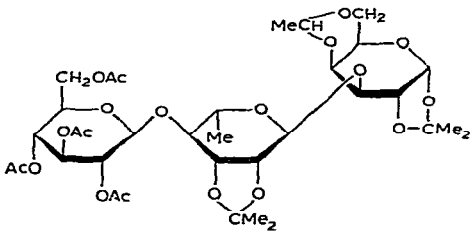

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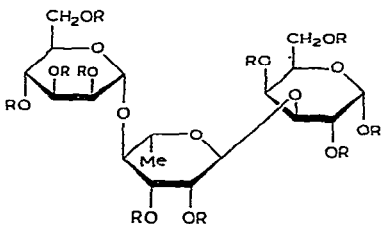

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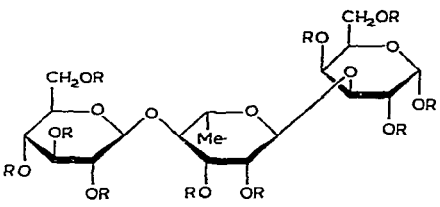

20 R = Ac
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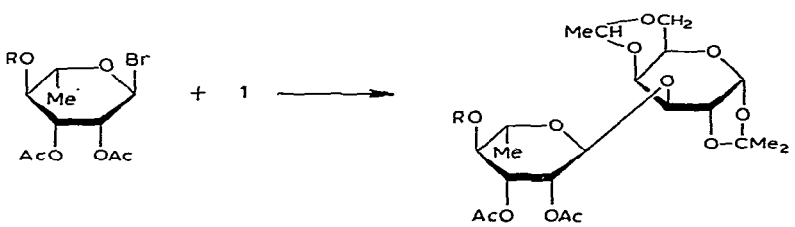
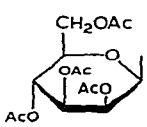
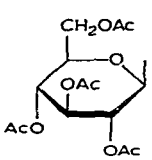
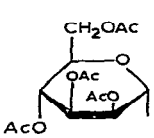


22 R =  23

24 R =  25

26 R =  27

matography) **23**, **25**, and **27** in yields of 75, 70, and 77%, respectively, calculated from **1**.

We have found that the order of addition of reagents and the use of anhydrous conditions are important in these syntheses, as well as in the synthesis of **2**; the solution of hexosylrhamnosyl bromide (rhamnopyranosyl bromide) must be added slowly to the mixture of the aglycon plus mercuric cyanide. Although highly reactive glycosyl bromides of this kind rapidly decompose when dissolved in acetonitrile alone or in admixture with nitromethane, such solutions can be stabilised by the addition of a small proportion of 2,6-lutidine or 2,4,6-collidine. This precaution is unnecessary for glycosylations with tetra-*O*-acetyl-α-D-mannopyranosyl and -α-D-glucopyranosyl bromides (syntheses of **16** and **17**).

Thus, glycosylation of secondary hydroxyl groups in **1** and **3** by glycosyl bromides of different reactivity proceeded with almost equal efficiency, and high yields of trisaccharide derivatives are obtainable by either way.

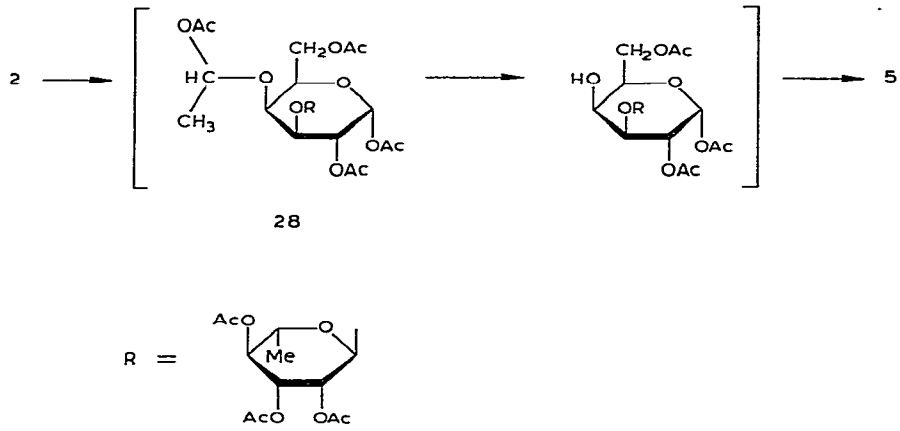
Transformation of these trisaccharide derivatives into the respective peracetates necessitated removal of the 4,6-*O*-ethylidene group from the galactose residue, which is the most stable of the protecting groups used. The search for conditions for its removal was performed with the disaccharide derivatives **2** and **4** as model compounds.

Treatment[7,8] of **4** with 80% acetic acid at 100° for 3 h followed by acetylation afforded (t.l.c.) mainly peracetates of rhamnose and galactose. Compound **2** gave (t.l.c.) a mixture of disaccharide peracetates and compound(s) still retaining the ethylidene group, as well as peracetates of rhamnose and galactose. A similar mixture of products was obtained when **2** was treated with 99% trifluoroacetic acid to remove the 1,2-*O*-isopropylidene group[7] followed by acetylation, hydrolysis with 80% acetic acid as mentioned above, and reacetylation. Column chromatography afforded 3-*O*-α-L-rhamnopyranosyl-D-galactose hepta-acetates, presumably an ~1:1 α,β-mixture (p.m.r. data), in 39% yield.

Attempts to remove the 4,6-*O*-ethylidene group by treatment with 90% trifluoroacetic acid at room temperature were unsuccessful; after 70 h, **2** gave a disaccharide derivative devoid of the 1,2-*O*-isopropylidene group only. In the high-field portion of the p.m.r. spectrum (CD_3OD) were present signals of equal integrated intensity corresponding to the methyl groups of three acetates (δ 2.12, 2.06, 1.95), the ethylidene group (δ 1.32, d, *J* 5 Hz), and rhamnose (δ 1.17, d, $J_{6,5}$ 7 Hz). No monosaccharide derivatives were detected (t.l.c.) after acetylation. Thus, direct hydrolysis with acid did not seem very promising for removal of the 4,6-*O*-ethylidene group from the galactopyranose residue.

In seeking an alternative approach, note was taken of (*a*) the higher acid-lability of acyclic acetals as compared with cyclic acetals[15] and (*b*) the ring-opening of the 4,6-*O*-ethylidene group in D-glucopyranose derivatives by acid-catalysed acetolysis[16,17]. Analogous behaviour of the D-galactopyranose acetal was expected, and a procedure was developed for the conversion of both **2** and **4** into **5**.

When the disaccharide **2** was treated with acetic acid–acetic anhydride con-



taining a catalytic amount of sulphuric acid for 15 h at room temperature, **28** was obtained, and characterised by p.m.r. spectroscopy (CCl_4) [δ 1.24 (d, 3 H, J 5 Hz, Me of Rha*p*), 1.52 (d, 3 H, J 5 Hz, Me of acetoxyethyl group), 1.95–2.16 (21 H, 7 AcO)]. The *O*-acetoxyethyl group apparently was attached to position 4 of the galactose moiety. Subsequent acid hydrolysis followed by acetylation quantitatively afforded **5**, whose structure was indicated by analytical and spectral data and by its conversion into the free disaccharide **6** in 90% yield.

This reaction sequence could be performed without isolation of the intermediates, and hence was very convenient from the preparative point of view. When applied to the trisaccharide derivatives **23**, **25**, and **27**, the procedure gave the α-deca-acetates **14**, **20**, and **18** in yields of 80, 80, and 72%, respectively.

For the disaccharide derivative **4**, an additional step, involving brief (5–10 min) treatment with 90% trifluoroacetic acid at room temperature, was introduced before applying the foregoing procedure; a quantitative yield of **5** was again attained. This procedure was applied to trisaccharide derivatives **16** and **17** and to **12** (following its decarbonylation and acetylation), to yield **18**, **20**, and **14** in yields of 76, 80, and 88%, respectively.

Analytical and spectral data for the peracetylated trisaccharides and the preparation of the unprotected trisaccharides **15**, **19**, and **21** in yields of 91, 94, and 97%, respectively, confirmed their structures.

EXPERIMENTAL

Optical rotations were determined with a Perkin–Elmer 141 polarimeter at 22 ±2° for solutions in chloroform. Melting points were determined with a Kofler apparatus and are uncorrected. P.m.r. spectra were recorded on Varian DA-60-IL and Tesla BS-497 (100 MHz, C.S.S.R.) spectrometers with tetramethylsilane as the internal standard. I.r. spectra were measured with a UR-10 spectrometer. Column chromatography was performed on Silica Gel L (100–250 μm, C.S.S.R.) with a gradient of benzene→ethyl acetate. T.l.c. was performed on Silica Gel LS (5–40 μm,

C.S.S.R.) with 1:1 (*A*) and 1:2 (*B*) benzene–ethyl acetate and 1:1 ethyl acetate–methanol (*C*). For detection, the plates were sprayed with 25% H_2SO_4 and heated for 5–7 min at ~150°. P.c. was performed by the descending method on Filtrak FN 11 paper with 6:4:3 1-butanol–pyridine–water, and sugars were detected with the KIO_4–$AgNO_3$–NaOH reagent[18]. Anion-exchange chromatography of unprotected sugars was performed on a 71-100A (C.S.S.R.) instrument, with a glass column (13 × 0.5 cm) packed with DAx4 (Durrum, U.S.A.) resin, and elution with sodium borate buffer (0.7M, pH 7.7) at 55° and a rate of 20 ml/h. Solutions were concentrated *in vacuo* at 40°. Acetonitrile was dried with $CaCl_2$, and distilled from $CaCl_2$ and then from CaH_2. Dichloromethane was washed with conc. H_2SO_4 and water, dried with $CaCl_2$, and distilled from CaH_2. Nitromethane was distilled from urea at 100 mmHg and then from CaH_2. All solvents were freshly distilled before use. 2,6-Lutidine and 2,4,6-collidine were distilled from KOH.

Silver oxide was prepared by adding a solution of silver nitrate (5.4 g) in water (50 ml) to a solution of NaOH (2 g) in water (20 ml) at 80°. The precipitate was washed by decantation with hot water (10 × 20 ml), cooled to room temperature, washed with ethanol (2 × 10 ml), anhydrous ethanol (2 × 20 ml), and anhydrous ether (2 × 10 ml), and dried *in vacuo* at 70° for 3 h. Yield: 3.2 g.

Silver perchlorate was prepared by stirring a mixture of silver oxide (2.5 g) and 30% perchloric acid (3.6 ml) for 1 h at room temperature. The precipitate was removed by filtration, the filtrate was evaporated, and dry benzene (3 × 50 ml) was added to, and evaporated from, the residue, which was then dried *in vacuo*. Yield: 3.5 g.

Mercuric cyanide was recrystallised from dry acetone and dried *in vacuo*; a 0.1M aqueous solution had pH 7.

4,6-O-Ethylidene-1,2-O-isopropylidene-α-D-galactopyranose (**1**). — A mixture of crystalline 4,6-*O*-ethylidene-D-galactose[19] (17 g), *p*-toluenesulphonic acid monohydrate (200 mg), 2,2-dimethoxypropane (100 ml), and acetone (1 litre) was stirred for 12 h at room temperature. Triethylamine (1 ml) was added and the mixture was evaporated. A solution of the thick residue in chloroform was passed through a short column of alumina, the column was washed with chloroform (700 ml), and the eluate was evaporated to dryness. The residue was dried *in vacuo* to give a colourless syrup (16 g) which crystallised from 1:1 ether–hexane (200 ml) to afford **1** (6 g). Evaporation of the mother liquor and crystallisation of the residue from the same solvents (1:2, 100 ml) gave more **1** (5 g; total yield, 50%), m.p. 75°, $[\alpha]_D$ +44.6° (*c* 1.85); lit.[19] m.p. 72–74° (hexane), $[\alpha]_D$ +58° (ethanol). The mother liquor was evaporated and column chromatography of the residue gave an additional amount (4.5 g) of syrupy **1**.

Preparation of acylglycosyl bromides. — 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide was obtained as described elsewhere[20]. 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl bromide, 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide, 4,6-di-*O*-acetyl-2,3-*O*-carbonyl-α-D-mannopyranosyl bromide (**10**), 2,3-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl)-α-L-rhamnopyranosyl bromide (**22**),

2,3-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-L-rhamnopyranosyl bromide (**24**), and 2,3-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-L-rhamnopyranosyl bromide (**26**) were obtained from the corresponding peracetates by the following general procedure.

To a mixture of acetyl bromide (136 ml), glacial acetic acid (100 ml), and acetic anhydride (4 ml) was slowly added water (33 ml), dropwise with cooling (~ −10°) and agitation. The resulting, viscous solution, which contains 40% (w/w) of hydrogen bromide and ~1% (w/w) of acetic anhydride, can be safely kept in a refrigerator.

To a solution of peracetate (7 mmol) in dry chloroform (40 ml) was added the foregoing solution (10 ml), and the mixture was kept for 30–45 min at room temperature, and then diluted with chloroform (100 ml) and poured into ice–water (300 ml). The aqueous layer was extracted with chloroform (25 ml), the combined organic layer and extract was washed with ice-cold, saturated, aqueous sodium hydrogencarbonate (2 × 100 ml), filtered through cotton, and evaporated. The residue was dried *in vacuo*, to yield the homogeneous (t.l.c., solvents *A* and *B*) bromide (95 ±3%) as a white solid suitable for glycosylation.

4,6-O-Ethylidene-1,2-O-isopropylidene-3-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-α-D-galactopyranose (**2**). — To a solution of **1** (1.23 g, 5.0 mmol) and mercuric cyanide (1.26 g, 5 mmol) in acetonitrile (10 ml) was added a solution of tri-*O*-acetyl-α-L-rhamnopyranosyl bromide (2.16 g, 6.5 mmol) in acetonitrile (10 ml) containing 0.1 ml of 2,6-lutidine, during 60 min, with stirring at room temperature. The mixture was diluted with 2:1 hexane–chloroform (150 ml) and washed with water (3 × 80 ml). The organic layer was concentrated, and the residue (3.16 g) was subjected to column chromatography to yield **2** (2.4 g, 92%) as a white solid, R_F 0.51 (*A*), $[\alpha]_D$ +1.5° (*c* 4.4). P.m.r. data ($CDCl_3$): δ 1.18 (d, 3 H, *J* 7.5 Hz, Me of Rha*p*), 1.32 (d, 3 H, *J* 5.5 Hz, *Me*CH), 1.35 and 1.47 (2 s, 6 H, CMe_2), 1.93, 2.00, and 2.10 (3 s, 9 H, 3 AcO), 4.66 (q, 1 H, *J* 5.5 Hz, MeC*H*), and 5.83 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 of Gal*p*).

Anal. Calc. for $C_{23}H_{34}O_{13}$: C, 53.27; H, 6.60. Found: C, 53.10; H, 6.57.

4,6-O-Ethylidene-1,2-O-isopropylidene-3-O-(2,3-O-isopropylidene-α-L-rhamnopyranosyl)-α-D-galactopyranose (**3**). — To a solution of **2** (6.0 g, 11.5 mmol) in dry methanol (50 ml) was added M methanolic sodium methoxide (0.5 ml). The mixture was kept for 1 h at room temperature, and then treated with M acetic acid in methanol (0.5 ml) and evaporated. The residue was dissolved in acetone (300 ml), 2,2-dimethoxypropane (15 ml), anhydrous copper sulphate (30 g), and *p*-toluenesulphonic acid monohydrate (200 mg) were added, and the mixture was shaken for 5 h at room temperature and then filtered through a layer of alumina. The filtrate was evaporated, and the residue was dried *in vacuo*, to give **3** as a white, hygroscopic solid (4.4 g, 88%), R_F 0.35 (*A*), $[\alpha]_D$ +31.5° (*c* 2.10). P.m.r. data ($CDCl_3$): δ 1.25 (d, 3 H, *J* 6 Hz, Me of Rha*p*), 1.33 (d, 3 H, *J* 4.5 Hz, *Me*CH), 1.35 and 1.54 (2 s, 6 H, CMe_2 of Gal*p*), 1.37 and 1.54 (2 s, 6 H, CMe_2 of Rha*p*), 4.63 (q, 1 H, *J* 4.5 Hz, MeC*H*), 5.17 (s, 1 H, H-1 of Rha*p*), and 5.64 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1 of Gal*p*).

Anal. Calc. for $C_{20}H_{32}O_{10}$: C, 55.54; H, 7.45. Found: C, 56.06; H, 7.80.

3-O-(4-O-Acetyl-2,3-O-isopropylidene-α-L-rhamnopyranosyl)-4,6-O-ethylidene-

1,2-O-isopropylidene-α-D-galactopyranose (**4**). — A solution of **3** (4.4 g, 10.2 mmol) in acetic anhydride–pyridine (1:1, 20 ml) was kept for 15 h at room temperature, ethanol (10 ml) was then added, and the mixture was stored for 0.5 h and then diluted with 1:2 chloroform–hexane (150 ml). The solution was washed successively with water (2 × 100 ml), saturated, aqueous sodium hydrogencarbonate (2 × 100 ml), and water (2 × 100 ml), and evaporated. 5:1:1 Toluene–ethanol–heptane (2 × 50 ml) was evaporated from the residue which was then dried to give **4** as a solid (4.5 g, 93%), R_F 0.53 (*A*), $[\alpha]_D$ +36.0° (*c* 1.73). This product was used in all subsequent syntheses. Crystallisation from methanol gave an analytical sample of **4**, m.p. 148–149°, $[\alpha]_D$ +38.0° (*c* 3.30). P.m.r. data ($CDCl_3$): δ 1.14 (d, 3 H, *J* 6 Hz, Me of Rha*p*), 1.38 (d, 3 H, *J* 5 Hz, *Me*CH), 1.35, 1.42, 1.55, and 1.57 (4 s, 12 H, 2 Me_2C), 2.12 (s, 3 H, AcO), 4.66 (q, 1 H, *J* 5 Hz, MeC*H*), 5.28 (s, 1 H, H-1 of Rha*p*), and 5.82 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 of Gal*p*).

Anal. Calc. for $C_{22}H_{34}O_{11}$: C, 55.68; H, 7.22. Found: C, 55.74; H, 7.07.

Compound **4** (1.2 g, 2.54 mmol) was dissolved in 0.01M methanolic sodium methoxide (20 ml), and the solution was kept at room temperature for 2 h and then evaporated to dryness. A solution of the residue in chloroform (100 ml) was washed with water (2 × 50 ml) and evaporated, and the residue was dried *in vacuo* to yield **3** (1.1 g, 100%), R_F 0.35 (*A*), $[\alpha]_D$ +30.0° (*c* 1.00).

Methyl 2,3-O-carbonyl-4,6-O-isopropylidene-α-D-mannopyranoside (**8**). — To a stirred suspension of methyl 4,6-*O*-isopropylidene-α-D-mannopyranoside[12] (4.2 g, 20 mmol) in dry 1,4-dioxane (50 ml) was added triethylamine (14 ml) followed by a solution of methyl chloroformate (5.6 ml, 60 mmol) in dry benzene (30 ml) dropwise during 1 h with ice-cooling. After 4 h at 0°, the mixture was diluted with chloroform (150 ml) and washed with water (4 × 100 ml). The organic layer was evaporated, and the residue was dried *in vacuo* and crystallised from ethanol (20 ml), to afford **8** (3.5 g, 74%), m.p. 122–124°, $[\alpha]_D$ +6.9° (*c* 2.20); ν_{max}^{KBr} 1800 cm^{-1} (C=O of carbonate). P.m.r. data ($CDCl_3$): δ 1.40 and 1.50 (2 s, 6 H, CMe_2), 3.37 (s, 3 H, OMe), and 5.00 (s, 1 H, H-1 of Man*p*).

Anal. Calc. for $C_{11}H_{16}O_7$: C, 50.76; H, 6.15. Found: C, 50.60; H, 6.01.

1,4,6-Tri-O-acetyl-2,3-O-carbonyl-α-D-mannopyranose (**9**). — To a solution of **8** (9 g, 3.8 mmol) in ethanol–chloroform (1:1, 80 ml) was added 90% trifluoroacetic acid (50 ml), and the mixture was kept for 5–10 min at room temperature. The solution was evaporated and 5:1:1 toluene–ethanol–heptane (2 × 100 ml) was evaporated from the residue, which was then dissolved in acetic anhydride (30 ml) and treated with 1% (v/v) conc. sulphuric acid in acetic anhydride (45 ml). The mixture was kept for 4 h at room temperature and then poured into ice–water (300 ml), stirred for 1 h, and extracted with chloroform (2 × 100 ml). The organic layer was washed successively with water (2 × 100 ml), saturated, aqueous sodium hydrogencarbonate (2 × 100 ml), and water (2 × 100 ml), and evaporated. The residue was crystallised from ethanol (50 ml) to give **9** (8.7 g, 71%), m.p. 115–117°, $[\alpha]_D$ +12.5° (*c* 1.50); lit.[11] m.p. 117.5–118.5° (ethanol), $[\alpha]_D$ +15.6° (chloroform).

3-O-[4-O-(4,6-Di-O-acetyl-2,3-O-carbonyl-β-D-mannopyranosyl)-2,3-O-isopro-

pylidene-α-L-rhamnopyranosyl]-*4,6-O-ethylidene-1,2-O-isopropylidene-α-D-galactopyranose* (**12**) *and its α anomer* (**11**). — A mixture of **3** (560 mg, 1.30 mmol), silver oxide (460 mg, 2 mmol), silver perchlorate (40 mg, 0.2 mmol), and powdered 4 Å molecular sieve (1 g) in dichloromethane (2 ml) was stirred at room temperature for 40 min. A solution of **10** (640 mg, 2 mmol) (obtained from **9**) in dichloromethane (8 ml) was added and the mixture was stirred at room temperature for 20 h. The solids were removed by filtration, and the combined filtrate and chloroform washings (3 × 10 ml) were washed successively with water (10 ml), saturated, aqueous sodium hydrogencarbonate (10 ml), and water (10 ml), and concentrated *in vacuo*. The resulting syrup (1.0 g), after column chromatography, yielded a syrupy mixture of **12** and **11** (740 mg, 82%), $[\alpha]_D$ −8.0° (*c* 2.60). This mixture was rechromatographed on silica gel to give **11** (40 mg, 4.4%), R_F 0.44 (*A*); a mixture of **11** and **12** (120 mg); and **12** (560 mg, 66%), R_F 0.38 (*A*).

Compound **11** was a colourless syrup, $[\alpha]_D$ +16.0° (*c* 1.6). P.m.r. data ($CDCl_3$): δ 1.20 (d, 3 H, *J* 6 Hz, Me of Rha*p*), 1.27–1.47 (15 H, alkylidenes), 2.04 and 2.06 (2 s, 6 H, 2 AcO), and 5.84 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 of Gal*p*).

Anal. Calc. for $C_{31}H_{44}O_{18}$: C, 52.83; H, 6.25. Found: C, 53.12; H, 6.52.

Compound **12** was a colourless syrup, $[\alpha]_D$ −11.8° (*c* 1.8). P.m.r. data ($CDCl_3$): δ 1.20 (d, 3 H, *J* 5 Hz, Me of Rha*p*), 1.28–1.48 (15 H, alkylidenes), 2.04 and 2.07 (2 s, 6 H, 2 AcO), and 5.85 (d, 1 H, *J* 4 Hz, H-1 of Gal*p*).

Anal. Calc. for $C_{31}H_{44}O_{18}$: C, 52.83; H, 6.25. Found: C, 52.61; H, 6.25.

4,6-O-Ethylidene-1,2-O-isopropylidene-3-O-[*2,3-O-isopropylidene-4-O-*(*2,3,4,6-tetra-O-acetyl-β-D-mannopyranosyl*)-*α-L-rhamnopyranosyl*]-*α-D-galactopyranose* (**13**). — Compound **12** (700 mg, 1 mmol) was treated with 0.2M methanolic sodium methoxide (5 ml) for 1 h at room temperature. After evaporation of the solvent, the residue was dissolved in 1:1 acetic anhydride–pyridine (5 ml) and kept for 15 h at room temperature. Methanol (2 ml) was added, and, after 30 min, the mixture was diluted with chloroform (50 ml) and washed with water (2 × 30 ml). The organic layer was evaporated to dryness, and 5:1:1 toluene–ethanol–heptane was evaporated several times from the residue, which was then dried *in vacuo* to yield the title compound (745 mg, 99%) as a white solid, R_F 0.47 (*A*), $[\alpha]_D$ −19.2° (*c* 1.3). P.m.r. data ($CDCl_3$): δ 1.16 (d, 3 H, *J* 5 Hz, Me of Rha*p*), 1.26–1.48 (15 H, alkylidenes), 1.96, 1.92, 2.00, and 2.08 (4 s, 12 H, 4 AcO), 4.60 (q, 1 H, *J* 5 Hz, MeC*H*), and 5.72 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 of Gal*p*).

Anal. Calc. for $C_{34}H_{50}O_{19}$: C, 53.61; H, 6.48. Found: C, 53.40; H, 6.49.

Analogous treatment of **11** (700 mg) afforded, after column chromatography, syrupy **16** (690 mg, 92%), R_F 0.46 (*A*), $[\alpha]_D$ +37.5° (*c* 1.70).

4,6-O-Ethylidene-1,2-O-isopropylidene-3-O-[*2,3-O-isopropylidene-4-O-*(*2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl*)-*α-L-rhamnopyranosyl*]-*α-D-galactopyranose* (**16**). — Compound **4** (1.2 g, 2.5 mmol) was treated with 0.01M methanolic sodium methoxide (10 ml) for 2 h at room temperature, 0.1M acetic acid in methanol (1.0 ml) was added, and the mixture was evaporated. Nitromethane (2 × 20 ml) was distilled from the residue, which was then dissolved in acetonitrile (10 ml). Mercuric cyanide

(750 mg, 3 mmol) and tetra-*O*-acetyl-α-D-mannopyranosyl bromide (1.65 g, 4 mmol) were added and the mixture was stirred for 2 h at room temperature. After dilution with chloroform (100 ml) and successive washing with water (100 ml), 0.5M aqueous potassium bromide (2 × 100 ml), and water (50 ml), the organic layer was evaporated and the resulting syrup was chromatographed, to yield **16** (1.41 g, 72%) as a white solid, R_F 0.46 (*A*), $[\alpha]_D$ +38.2° (*c* 1.53). P.m.r. data (CCl_4): δ 1.22 (d, 3 H, *J* 6 Hz, Me of Rha*p*), 1.28–1.50 (15 H, alkylidenes), 1.94, 1.97, 2.01, and 2.12 (4 s, 12 H, 4 AcO), 4.61 (q, 1 H, *J* 5 Hz, MeC*H*), and 5.72 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 of Gal*p*). Crystallisation from benzene–hexane afforded the analytical sample of **16**, m.p. 169–171°, $[\alpha]_D$ +36.4° (*c* 2.20).

Anal. Calc. for $C_{34}H_{50}O_{19}$: C, 53.61; H, 6.48. Found: C, 53.67; H, 6.54.

4,6-O-Ethylidene-1,2-O-isopropylidene-3-O-[2,3-O-isopropylidene-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-L-rhamnopyranosyl]-α-D-galactopyranose (**17**). — This compound, obtained from **4** (1.2 g) and tetra-*O*-acetyl-α-D-glucopyranosyl bromide (1.65 g) in the presence of mercuric cyanide (750 mg) as described above, was a chromatographically homogeneous solid (1.61 g, 81%), R_F 0.48 (*A*), $[\alpha]_D$ +10.4° (*c* 3.1). P.m.r. data (CCl_4): δ 1.18 (d, 3 H, *J* 6 Hz, Me of Rha*p*), 1.26–1.49 (15 H, alkylidenes), 1.96, 1.98, 2.02 (× 2) (3 s, 12 H, 4 AcO), 4.59 (q, 1 H, *J* 5 Hz, MeC*H*), and 5.70 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 of Gal*p*).

Anal. Calc. for $C_{34}H_{50}O_{19}$: C, 53.61; H, 6.48. Found: C, 53.17; H, 6.72.

3-O-[2,3-Di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-α-L-rhamnopyranosyl]-4,6-O-ethylidene-1,2-O-isopropylidene-α-D-galactopyranose (**27**). — To a solution of **1** (2.0 g, 8.1 mmol) and mercuric cyanide (2.5 g, 8.1 mmol) in acetonitrile (15 ml) was added dropwise, during 1 h with stirring, a solution of **26** [6.7 g, 10.4 mmol; prepared from 1,2,3-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-L-rhamnopyranose[21] (6.5 g, 10.5 mmol)] in 1:1 acetonitrile–nitromethane (15 ml) containing 2,4,6-collidine (0.1 ml). The mixture was diluted with chloroform (200 ml) and washed successively with water (100 ml), 0.5M aqueous potassium bromide (2 × 100 ml), and water (100 ml). The organic layer was evaporated to a syrup, which was chromatographed to give **27** as a solid (5.1 g, 77%), R_F 0.33 (*A*), $[\alpha]_D$ +20.4° (*c* 1.87). P.m.r. data (CCl_4): δ 1.18–1.46 (12 H, Me of Rha*p* and alkylidenes), 1.96, 2.01 (× 2), 2.08 (× 2), and 2.14 (4 s, 18 H, 6 AcO), and 5.78 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 of Gal*p*).

Anal. Calc. for $C_{35}H_{50}O_{21}$: C, 52.12; H, 6.24. Found: C, 51.82; H, 6.21.

3-O-[2,3-Di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-mannopyranosyl)-α-L-rhamnopyranosyl]-4,6-O-ethylidene-1,2-O-isopropylidene-α-D-galactopyranose (**23**). — This compound, obtained from **1** (1.2 g, 5.0 mmol), bromide **22** (4.0 g, 6.3 mmol) [prepared from 1,2,3-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl)-α-L-rhamnopyranose[11] (4.0 g, 6.5 mmol)], and mercuric cyanide (1.3 g, 5.0 mmol), as described above, was a solid (3.05 g, 75%), R_F 0.30 (*A*), $[\alpha]_D$ −27.2° (*c* 2.80); lit.[8] glassy powder, m.p. 87–92°, $[\alpha]_D^{25}$ −23° (*c* 1, chloroform).

3-O-[2,3-Di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-L-rhamnopyranosyl]-4,6-O-ethylidene-1,2-O-isopropylidene-α-D-galactopyranose (**25**). —

This compound, prepared analogously from **1** (1.2 g), bromide **24** (4.1 g) [prepared from scillabiose hepta-acetate[22] (4.0 g)], and mercuric cyanide (1.2 g), was a solid (2.82 g, 70%), R_F 0.36 (*A*), $[\alpha]_D$ −17.0° (*c* 2.00); lit.[7] amorphous powder, m.p. 104–108°, $[\alpha]_D^{25}$ −25° (*c* 1, chloroform).

3-O-α-L-Rhamnopyranosyl-D-galactose hepta-acetate. — A solution of **2** (1.55 g, 2.9 mmol) in a mixture of chloroform (45 ml) and 99% trifluoroacetic acid (5 ml) was kept at room temperature for 40 min and then concentrated. 5:1:1 Toluene–ethanol–heptane (2 × 30 ml) was evaporated from the residue, which was then treated with 1:1 acetic anhydride–pyridine (10 ml) for 15 h at room temperature. The mixture was evaporated, 5:1:1 toluene–ethanol–heptane was distilled from the residue, acetic acid (12 ml) and water (3 ml) were added to the residue, and the solution was heated at 100° for 3 h. The solvent was evaporated and 5:1:1 toluene–ethanol–heptane was distilled from the residue, which was then treated with acetic anhydride–pyridine as described above. Methanol (3 ml) was added, and the mixture was kept at room temperature for 0.5 h, diluted with chloroform (100 ml), and washed with water (5 × 70 ml). Evaporation of solvent and column chromatography of the residue yielded the syrupy title product (700 mg, 39%), R_F 0.50 (*A*), $[\alpha]_D$ +7.6° (*c* 1.72); lit.[9] $[\alpha]_D^{19}$ +14.6° (*c* 2.23, chloroform). P.m.r. data (CCl_4): δ 1.18 (d, 3 H, *J* 6 Hz, Me of Rha*p*), 1.95, 2.00, 2.02, 2.06, 2.10, 2.12, and 2.22 (7 s, 21 H, 7 AcO), 5.50 (d, ~0.5 H, *J* 8 Hz, H-1 of Gal*p*), and 6.22 (d, ~0.5 H, $J_{1,2}$ 4 Hz, H-1 of Gal*p*).

1,2,4,6-Tetra-O-acetyl-3-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-α-D-galactopyranose (**5**). — (*a*) A solution of **2** (1.5 g, 2.9 mmol) in a mixture of acetic anhydride (6 ml) and a solution (1.5 ml) of conc. sulphuric acid in acetic acid [prepared by addition of conc. sulphuric acid (0.1 ml) to acetic acid (25 ml)] was kept for 15 h at room temperature. Water (3 ml) was added to the mixture, which was then heated at 80° for 30 min. The solvents were removed and 5:1:1 toluene–ethanol–heptane (2 × 20 ml) was distilled from the residue, which was then treated with acetic anhydride (4 ml) for 1 h at room temperature. The mixture was shaken with water (60 ml) for 1 h and then extracted with chloroform (2 × 50 ml). The combined extracts were washed successively with water (2 × 70 ml), saturated, aqueous sodium hydrogencarbonate (2 × 100 ml), and water (70 ml), and evaporated to a residue, which was dried *in vacuo* to yield **5** as a homogeneous syrup, (1.75 g, 98%), R_F 0.50 (*A*), $[\alpha]_D$ +26.1° (*c* 2.44). P.m.r. data (CCl_4): δ 1.21 (d, 3 H, *J* 6 Hz, Me of Rha*p*), 1.96, 2.00, 2.02 (× 2), 2.12 (× 2), and 2.21 (5 s, 21 H, 7 AcO), and 6.26 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 of Gal*p*).

Anal. Calc. for $C_{26}H_{36}O_{17}$: C, 50.32; H, 5.85. Found: C, 50.27; H, 5.92.

(*b*) To a solution of **4** (475 mg, 1.0 mmol) in chloroform (1 ml) were added 90% trifluoroacetic acid (3 ml) and ethanol (1 ml), and the mixture was kept for 5–10 min at room temperature. The solvents were evaporated and 5:1:1 toluene–ethanol–heptane (3 × 20 ml) was evaporated from the residue, which was then dried *in vacuo* and processed as described in (*a*), to yield **5** as a homogeneous syrup

(620 mg, 100%), R_F 0.50 (*A*), $[\alpha]_D$ +30.0° (*c* 4.34). The p.m.r. spectrum was identical with that of **5** obtained from **2**.

1,2,4,6-Tetra-O-*acetyl-3*-O-[*2,3-di*-O-*acetyl-4*-O-(*2,3,4,6-tetra*-O-*acetyl-β*-D-*mannopyranosyl*)-α-L-*rhamnopyranosyl*]-α-D-*galactopyranose* (**14**). — Compound **14**, prepared from **23** (5.0 g) as described above (*a*) for **5**, was obtained (after column chromatography) as a syrup (4.5 g, 80%), R_F 0.56 (*B*), $[\alpha]_D$ −1.0° (*c* 2.87); lit.[8] $[\alpha]_D^{25}$ −4° (chloroform). P.m.r. data ($CDCl_3$): δ 1.31 (d, 3 H, *J* 6 Hz, Me of Rha*p*), 1.98, 2.00, 2.04, 2.07, 2.10, 2.11, and 2.15 (30 H, acetates), and 6.31 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 of Gal*p*).

1,2,4,6-Tetra-O-*acetyl-3*-O-[*2,3-di*-O-*acetyl-4*-O-(*2,3,4,6-tetra*-O-*acetyl-β*-D-*glucopyranosyl*)-α-L-*rhamnopyranosyl*]-α-D-*galactopyranose* (**20**). — Compound **20** was obtained from **25** (4.4 g), as described above, as a homogeneous syrup (4.0 g, 80%), R_F 0.58 (*B*), $[\alpha]_D$ +6.3° (*c* 1.87); lit.[7] $[\alpha]_D^{20}$ +6.2° (chloroform). P.m.r. data ($CDCl_3$): δ 1.30 (d, 3 H, *J* 6 Hz, Me of Rha*p*), 1.94, 1.98, 2.01, 2.04, 2.07, 2.09, 2.10, and 2.16 (30 H, acetates), and 6.23 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 of Gal*p*).

1,2,4,6-Tetra-O-*acetyl-3*-O-[*2,3-di*-O-*acetyl-4*-O-(*2,3,4,6-tetra*-O-*acetyl-α*-D-*mannopyranosyl*)-α-L-*rhamnopyranosyl*]-α-D-*galactopyranose* (**18**). — Compound **18** was obtained from **27** (4.0 g), as described above, as a syrup (3.3 g, 72%), R_F 0.59 (*B*), $[\alpha]_D$ +31.8° (*c* 1.67). P.m.r. data ($CDCl_3$): δ 1.42 (d, 3 H, *J* 6 Hz, Me of Rha*p*), 2.00, 2.04, 2.07, 2.10, 2.13, 2.16, and 2.21 (30 H, acetates), and 6.34 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 of Gal*p*).

Anal. Calc. for $C_{38}H_{52}O_{25}$: C, 50.22; H, 5.77. Found: C, 50.24; H, 6.21.

The trisaccharide deca-acetates **14**, **18**, and **20** were obtained, as described above (*b*) for **5** (followed by column chromatography), from **13**, **16**, and **17**, respectively, in yields of 88, 76, and 80%. The p.m.r. spectra and $[\alpha]_D$ values of these products were identical with those of **14**, **18**, and **20** described above.

3-O-α-L-*Rhamnopyranosyl*-D-*galactose* (**6**). — Compound **5** (200 mg) was treated with 0.01 M methanolic sodium methoxide (10 ml) for 45–60 min at room temperature. The solution was made neutral with KU-2 (H^+) resin, the filtrate was evaporated to dryness, and a solution of the residue in water (2 ml) was lyophilised to give **6** (95 mg, 90%), R_F 0.69 (t.l.c., solvent *C*), R_{Gal} 0.85 (p.c.), $[\alpha]_D$ +8.1° (equil.; *c* 1.30, water), $[\alpha]_D$ −10.5° (equil.; *c* 1.85, methanol); lit.[9] $[\alpha]_D^{23}$ −7.6° (equil.; methanol).

O-*β*-D-*Mannopyranosyl*-(*1→4*)-O-α-L-*rhamnopyranosyl*-(*1→3*)-D-*galactose* (**15**), O-α-D-*mannopyranosyl*-(*1→4*)-O-α-L-*rhamnopyranosyl*-(*1→3*)-D-*galactose* (**19**), *and* O-*β*-D-*glucopyranosyl*-(*1→4*)-O-α-L-*rhamnopyranosyl*-(*1→3*)-D-*galactose* (**21**). — These compounds were obtained, as described above, from **14**, **18**, and **20**, respectively: **15** [100 mg (91%) from **14** (200 mg)], R_F 0.42 (t.l.c., solvent *C*), R_{Gal} 0.39 (p.c.), $[\alpha]_D$ −15.2° (equil.; *c* 1.75, water) {lit.[8] $[\alpha]_D^{25}$ −13° (*c* 0.5, water)}; **19** [240 mg (94%) from **18** (470 mg)], R_F 0.48 (t.l.c., solvent *C*), R_{Gal} 0.55 (p.c.), $[\alpha]_D$ +27.2° (equil.; *c* 2.3, water) {lit.[6] $[\alpha]_D^{20}$ +22° (*c* 0.57, water)}; **21** [350 mg (97%) from **20** (660 mg)], R_F 0.48 (t.l.c., solvent *C*), R_{Gal} 0.58 (p.c.), $[\alpha]_D$ −0.1° (equil.; *c* 1.55, water), $[\alpha]_D$ −14.0° (equil.; *c* 1.00, methanol) {lit.[7] $[\alpha]_D^{20}$ −19° (*c* 0.5, methanol)}.

Compounds **15**, **19**, and **21** were homogeneous by anion-exchange chromatography, and had elution times of 60, 92, and 80 min, respectively.

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