Carbohydrate Research, 150 (1986) 187–197
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS OF THE TETRASACCHARIDE REPEATING-UNIT OF THE LIPOPOLYSACCHARIDE ISOLATED FROM *Pseudomonas maltophilia**

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(Received October 23rd, 1985; accepted for publication, December 20th, 1985)

ABSTRACT

The title tetrasaccharide having the structure 3-*O*-Me-β-L-Xyl*p*-(1→4)-α-L-Rha*p*-(1→4)-α-L-Rha*p*-(1→2)-L-Rha*p* was obtained by reaction of the α-acetobromo derivative of 4-*O*-(3-*O*-methyl-β-L-xylopyranosyl)-L-rhamnopyranose and benzyl 3,4-di-*O*-benzyl-2-*O*-(2,3-*O*-isopropylidene-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside, followed by removal of the protecting groups. The synthesised compounds were characterised on the basis of n.m.r. data.

INTRODUCTION

Pseudomonas maltophilia is an opportunist pathogen and the repeating unit[1] of the lipopolysaccharide is composed of one 3-*O*-methyl-L-xylose and three L-rhamnose residues. We have described[2] an economic synthesis of 3-*O*-methyl-L-xylose, starting from D-glucose, and demonstrated the easy preparation of various di-[3,4] and tri-rhamnosides[5] having different bond-types. We now report the synthesis of the tetrasaccharide repeating-unit.

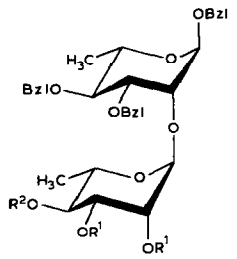
RESULTS AND DISCUSSION

Our first approach to the title tetrasaccharide involved a step-wise synthesis starting from the reducing end. Benzyl 3,4-di-*O*-benzyl-α-L-rhamnopyranoside, easily obtained either by the hydrogenolysis[6] of dioxolane-type benzylidene acetals or by phase-transfer alkylation[7], was rhamnosylated, using $Hg(CN)_2$ as acid acceptor and promotor (Helferich conditions), and gave the crystalline disaccharide derivative **1**. Zemplén deacetylation of **1** gave **2**, which had been synthesised[8] previously without the isolation of the intermediate **1**. Treatment of **2** with 2,2-dimethoxypropane[9] in the presence of toluene-*p*-sulphonic acid gave the disaccharide

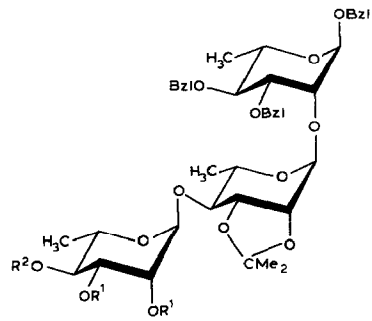
*Dedicated to Professor N. K. Kochetkov.

0008-6215/86/$ 03.50

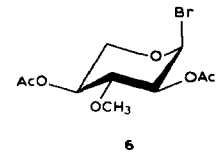
derivative **3** having HO-4′ unsubstituted. Rhamnosylation of **3** then gave the trirhamnoside derivative **4** in which the α configuration of the newly formed interglycosidic bond was indicated by the $^1J_{C,H}$ value of 171.2 Hz and by the diagnostic chemical shifts[10,11] of the signals of C-3″ and C-5″. Zemplén deacetylation of **4** was followed by conversion of the product into the 2″,3″-*O*-isopropylidene derivative **5**, which was glycosylated with 2,4-di-*O*-acetyl-3-*O*-methyl-α-L-xylopyranosyl bromide (**6**). The coupling reaction was effective, but the stereoselectivity was poor ($\alpha\beta$-ratio 15:85; ^{1}H-n.m.r. data) and the anomers could not be separated.



1 $R^1 = R^2 =$ Ac
2 $R^1 = R^2 =$ H
3 $R^1, R^1 = >CMe_2$; $R^2 =$ H



4 $R^1 = R^2 =$ Ac
5 $R^1, R^1 = >CMe_2$, $R^2 =$ H



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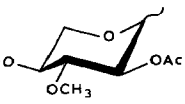


7 $R^1, R^1 = >CMe_2$, $R^2 =$ AcO

A two-plus-two block synthesis was then investigated using **3** as the aglycon. The glycosylation agent was prepared as follows. Benzyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside[12] was treated with **6** under Helferich conditions, but gave an ~2:8 $\alpha\beta$-mixture. The β anomer (**9**) could be crystallised from this mixture and the α anomer (**8**) was obtained by column chromatography. Unambigous ^{13}C-n.m.r. assignments were made using 2D methods. The ^{1}H-n.m.r. (200 MHz) spectra of these compounds were assigned with the aid of homonuclear shift-correlation (COSY) spectroscopy[13], and various types of 2D heteronuclear shift-correlation experiments[14,15] were used to establish the assignments given in Table I.

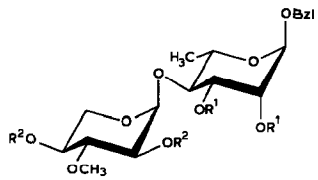
The isopropylidene groups were removed from **8** and **9** by acid hydrolysis and the products were acetylated to give the benzyl glycoside derivatives **10** and **11**, respectively. Deacetylation then gave the benzyl disaccharides (**12** and **13**). Hydrogenolysis (Pd/C) of **11** followed by acetylation and treatment with HBr gave the glycosyl bromide **14**, which reacted with **3** to give the tetrasaccharide derivative **15**; the corresponding β anomer could not be detected (chromatography, ^{1}H-n.m.r. spectroscopy).

The isopropylidene group was removed from **15** by acid hydrolysis, the benzyl groups in the product were hydrogenolysed, and acetylation then gave the tetra-

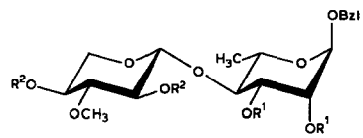
TABLE I

^{13}C-N.M.R. CHEMICAL SHIFT DATA (P.P.M.)

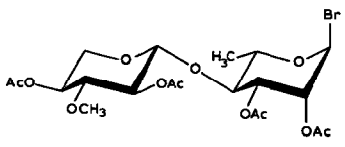
Unit	*Carbons*	**8**	**9**	**10**	**11**	**12**	**13**	**16**	**17**
	1							91.98	92.97
	2							74.94	79.60
R	3							68.97	70.49
	4							70.81	72.82
	5							62.85	69.23
	6							17.79	16.80
	1							99.38	102.26
	2							70.41	71.00
R′	3							70.16	71.07
	4							79.15	80.33
	5							68.13	68.46
	6							17.49	17.60
	1	96.28	96.20	100.84	100.97	99.51	100.02	99.11	101.55
	2	76.17	76.20	70.42	70.56	70.42	70.50	70.06	68.93
R″	3	76.96	76.91	69.41	69.37	71.26	71.21	70.87	69.23
	4	81.20	81.61	79.49	79.56	81.17	81.30	78.76	82.06
	5	67.40	64.71	67.42	67.50	62.37	62.40	68.92	68.78
	6	17.25	17.21	17.66	17.58	17.46	17.41	17.49	17.23
	1	96.60	100.01	96.56	100.46	100.86	103.87	100.43	103.78
	2	70.63	70.32	70.67	70.29	71.52	72.91	69.23	72.96
X	3	78.40	78.10	78.46	78.20	83.09	85.60	77.79	85.57
	4	69.57	69.11	69.63	69.25	68.76	67.86	70.08	67.86
	5	61.28	60.84	61.28	60.87	62.30	65.39	60.88	65.39



8 $R^1, R^1 = >CMe_2, R^2 = Ac$
10 $R^1 = R^2 = Ac$
12 $R^1 = R^2 = H$



9 $R^1, R^1 = >CMe_2, R^2 = Ac$
11 $R^1 = R^2 = Ac$
13 $R^1 = R^2 = H$



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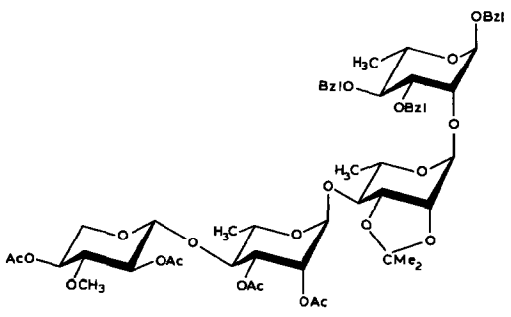

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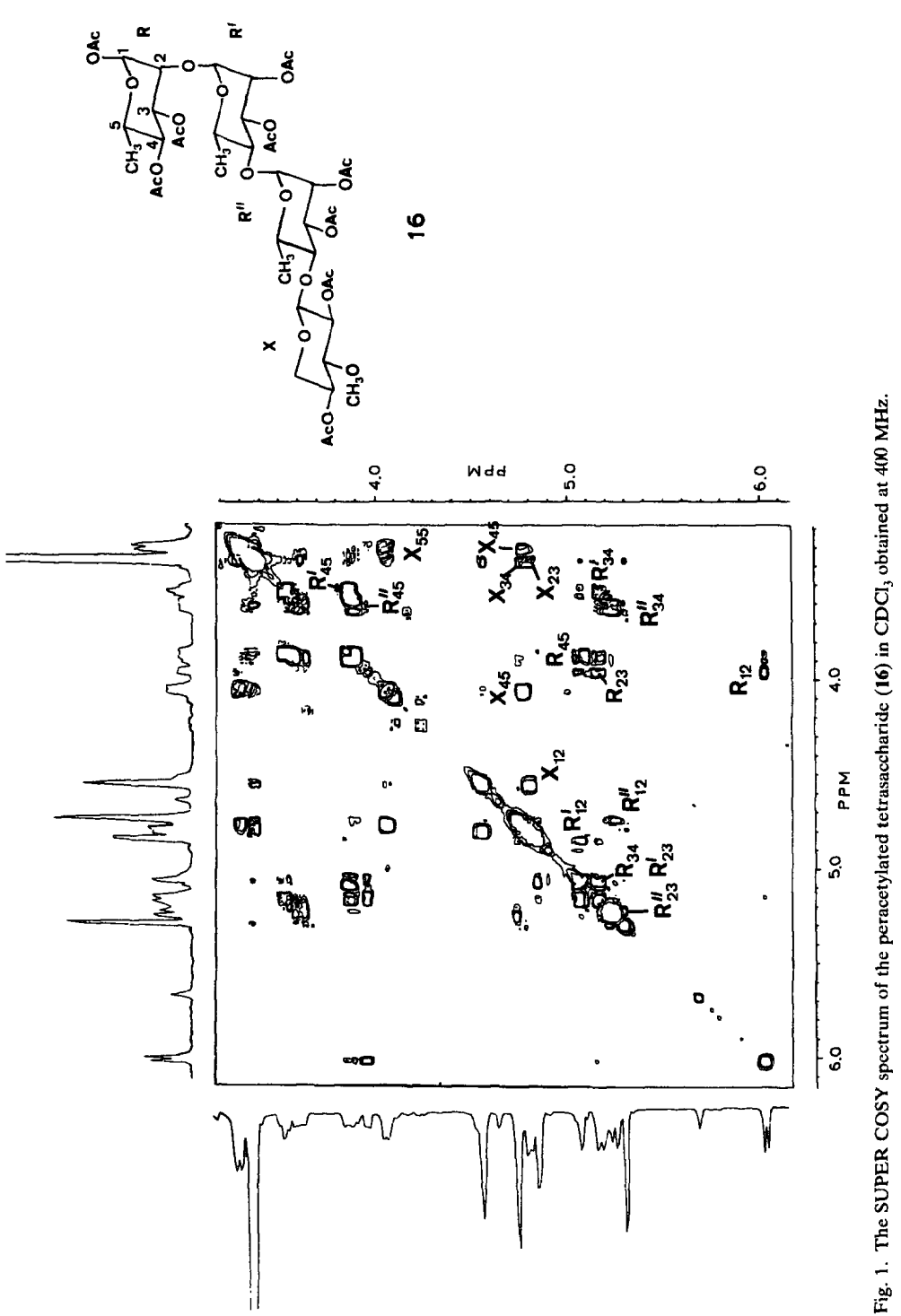


Fig. 1. The SUPER COSY spectrum of the peracetylated tetrasaccharide (**16**) in $CDCl_3$ obtained at 400 MHz.

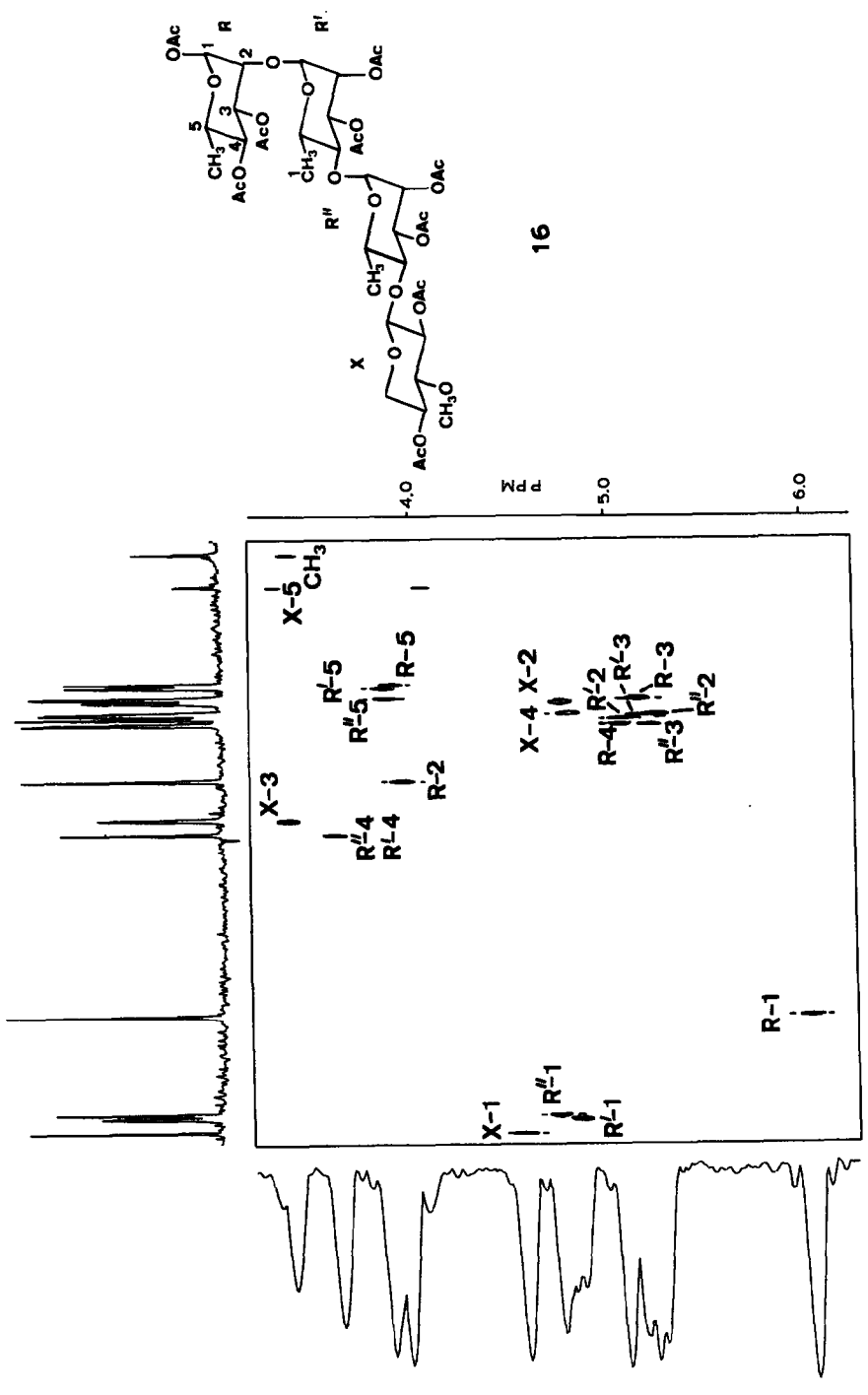


Fig. 2. Homonuclear broad-band-decoupled heteronuclear shift-correlation spectrum of **16**.

TABLE II

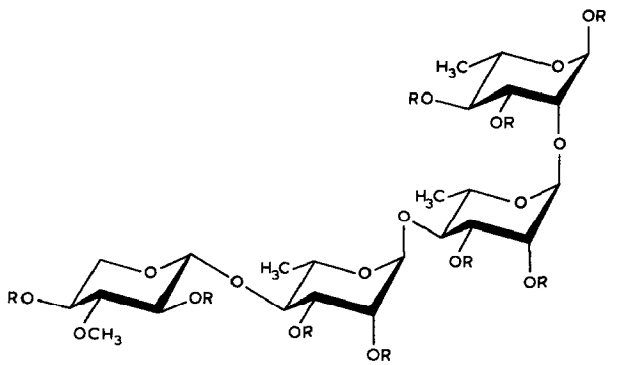
^{1}H-N.M.R. DATA FOR COMPOUND **16**

	Chemical shifts (δ)						*Coupling constants (Hz)*						
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6(5')*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{4,5'}$	$J_{5,5'}$
R	6.025	3.963	5.165	5.073	3.899	1.22	2.4	3.0	9.2	10.0	6.2		
R'	4.851	5.068	5.160	3.543	3.873	1.28	2.0	3.5	9.5	9.4	6.2		
R"	4.748	5.256	5.213	3.623	3.878	1.31	1.8	3.4	9.6	9.6	6.2		
X	4.565	4.808	3.381	4.773	4.066	3.313	5.0	6.8	6.4	4.0		5.9	12.3

saccharide derivative **16**. The ^{1}H-n.m.r. spectrum of **16** was analysed using the SUPER COSY[16] homonuclear shift-correlation method at 400 MHz (see Figs. 1 and 2).

The data given in Table II demonstrate that those protons which are on the glycosylated or methylated carbons resonate at the highest field. Although it has been well demonstrated that high-field 1D[17] and medium-field 2D[18] ^{1}H-n.m.r. spectra, as well as such 2D ^{13}C-n.m.r. methods as INEPT[19] or DEPT[20], are suitable for the determination of the bond types in unsubstituted oligosaccharides, our present result shows that acetylated oligosaccharides can also be used in structure analysis. The 2D heteronuclear shift-correlation experiment[15] resulted in the complete assignment of the ^{13}C-n.m.r. data. Comparing the data for **16** with those for the deacetylated product **17** shows that the chemical shifts of the signals of the glycosylated or methylated carbons are at a higher field than in **17**, most probably because of the unpredictable, negative β-shift values of the acetyl substituents.

Analysis of the spectrum of **17**, which contained 24 well-separated lines, was interpreted on the basis of data for methyl *O*-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside[5] and by comparison with the spectrum of **13**.



16 R = Ac

17 R = H

EXPERIMENTAL

General methods. — Melting points were determined on a Kofler hot-stage and are uncorrected. Optical rotations were measured with a Perkin–Elmer Model 241 automatic polarimeter. All reactions were monitored by t.l.c. on silica gel G (Merck) with detection by charring with sulfuric acid. N.m.r. spectra (internal Me_4Si) were recorded with a Bruker WP-200 SY (^1H, 200 MHz) or 400 AM (^1H, 400 MHz) spectrometer operating in the Fourier-transform mode.

Benzyl 3,4-di-O-benzyl-2-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**1**). — A solution of benzyl 3,4-di-*O*-benzyl-α-L-rhamnopyranoside[6] (2.62 g, 6 mmol) in dry acetonitrile (15 mL) was treated with 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide (3.19 g, 11.6 mmol) in the presence of powdered $Hg(CN)_2$ (2.29 g, 9 mmol). The mixture was stirred for 24 h at room temperature and worked-up conventionally. The product was crystallised from cyclohexane to give **1** (2.93 g, 68.8%), m.p. 102–104°, $[\alpha]_D$ −69.5° (*c* 0.8, chloroform), R_F 0.62 (dichloromethane–acetone, 95:5). ^1H-N.m.r. data ($CDCl_3$): δ 7.4–7.2 (m, 15 H, 3 Ph), 4.89 (d, 1 H, *J* 1.5 Hz, H-1), 4.78 (d, 1 H, *J* 1.5 Hz, H-1′), 2.08, 2.04, and 1.99 (3 s, 9 H, 3 OAc), 1.33 and 1.08 (2 d, 6 H, Me-5,5′).

Anal. Calc. for $C_{39}H_{46}O_{12}$: C, 71.10; H, 7.04. Found: C, 71.35; H, 7.09.

Benzyl 3,4-di-O-benzyl-2-O-α-L-rhamnopyranosyl-α-L-rhamnopyranoside (**2**). — A solution of **1** (2.5 g) in dry methanol (50 mL) was treated with NaOMe (5 mg) for 24 h, then neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated to give syrupy **2** (1.95 g, 88.5%), $[\alpha]_D$ −57° (*c* 0.8, chloroform), R_F 0.71 (dichloromethane–methanol, 9:1); lit.[8] $[\alpha]_D$ −55.6° (*c* 0.6, chloroform).

Benzyl 3,4-di-O-benzyl-2-O-(2,3-O-isopropylidene-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**3**). — A solution of **2** (3.0 g, 1.93 mmol) in 2,2-dimethoxypropane (5.2 g, 5 mmol) was stirred in the presence of toluene-*p*-sulphonic acid (100 mg) for 1.5 h at 20°. T.l.c. then showed the complete conversion of **2** into **3**. The mixture was diluted with dichloromethane (50 mL), solid $NaHCO_3$ (200 mg) was added, and the organic phase was washed with water (3 × 20 mL), dried (Na_2SO_4), and concentrated. The residue was crystallised from cyclohexane–hexane to give **3** (2.2 g, 68.7%), m.p. 102°, $[\alpha]_D$ −49° (*c* 1.2, chloroform), R_F 0.69 (dichloromethane–acetone, 9:1).

Anal. Calc. for $C_{36}H_{44}O_9$: C, 69.66; H, 7.14. Found: C, 70.02; H, 7.12.

Benzyl 3,4-di-O-benzyl-2-O-[2,3-O-isopropylidene-4-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl]-α-L-rhamnopyranoside (**4**). — A solution of **3** (1.5 g, 2.4 mmol) and $Hg(CN)_2$ (910 mg, 3.6 mmol) in benzene–nitromethane (1:1, 120 mL) was concentrated to 60 mL at atmospheric pressure and then cooled to room temperature. To the solution was added 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide (0.75 g, 2.1 mmol), and the mixture was stirred, with exclusion of moisture. After 20 min, more (0.75 g, 2.1 mmol) glycosyl bromide was added and stirring was continued for 24 h. The mixture was then diluted with chloroform (100 mL) and filtered. The organic layer was washed with M potassium

iodide (4 × 30 mL) and water, dried, and concentrated. Column chromatography (dichloromethane–ethyl acetate, 9:1) of the resulting syrup gave **4** (1.6 g, 74.1%), isolated as a syrup, $[\alpha]_D$ −55° (*c* 0.5, chloroform), R_F 0.65. ^{13}C-N.m.r. data: δ 109.4 (CMe_2), 98.8, 98.0, 96.0 (anomeric carbons), 75.3, 75.2, 68.9 (benzylic carbons), 27.9 and 26.5 (CMe_2), 18.0, 17.8 and 17.4 (CH_3 rhamnoses).

Anal. Calc. for $C_{48}H_{60}O_{16}$: C, 64.56; H, 6.77. Found: C, 65.02; H, 6.85.

*Benzyl 3,4-di-*O*-benzyl-2-*O*-[2,3-*O*-isopropylidene-4-*O*-(2,3-*O*-isopropylidene-α-*L*-rhamnopyranosyl)-α-*L*-rhamnopyranosyl]-α-*L*-rhamnopyranoside* (**5**). — Compound **4** (1.5 g, 1.68 mmol) was deacetylated with methanol (15 mL) containing sodium methoxide (10 mg). When the reaction was complete (t.l.c.), the solution was neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. The residue was dissolved in 2,2-dimethoxypropane (6 mL) and treated with toluene-*p*-sulphonic acid (100 mg); the isopropylidenation was monitored by t.l.c. After 1 h, the mixture was treated with solid $NaHCO_3$ (500 mg), diluted with dichloromethane (50 mL), washed with water (3 × 50 mL), dried, and concentrated. Column chromatography (dichloromethane–acetone, 9:1) of the residue gave **5** (1.24 g, 91.5%), isolated as a syrup, $[\alpha]_D$ −51° (*c* 1.9, chloroform), R_F 0.70. ^{13}C-N.m.r. data: δ 109.4 (2 CMe_2), 98.9, 98.0 and 95.8 (anomeric carbons), 75.3, 72.3, and 68.8 (3 CH_2Ph), 28.1, 27.9, 26.5, and 26.2 (2 CMe_2), 18.0, 17.6, and 17.0 (rhamnopyranoside Me).

Anal. Calc. for $C_{45}H_{58}O_{13}$: C, 66.98; H, 7.24. Found: C, 67.14; H, 7.19.

*2,4-Di-*O*-acetyl-3-*O*-methyl-α-*L*-xylopyranosyl bromide* (**6**). — 3-*O*-Methyl-L-xylose (3.28 g, 20 mmol) was treated with pyridine (15 mL) and acetic anhydride (15 mL) for 24 h. The mixture was then concentrated and a solution of the residue in dichloromethane (50 mL) was washed with M sulfuric acid (2 × 20 mL) and water (5 × 20 mL), dried, and concentrated. A solution of the syrupy acetate in dichloromethane (7 mL) was treated with acetic acid–HBr (3.5 mL) for 45 min at room temperature, then diluted with dichloromethane (200 mL), washed with water until neutral, dried, and concentrated. Recrystallisation of the residue from isopropyl ether gave **6** (4.15 g, 66.7%), m.p. 68°, $[\alpha]_D$ −169.5° (*c* 0.5, chloroform), R_F 0.76 (dichloromethane–acetone, 93:7).

Anal. Calc. for $C_{10}H_{15}BrO_6$: C, 38.60; H, 4.86; Br, 25.68. Found: C, 38.76; H, 4.91; Br, 25.91.

*Benzyl 3,4-di-*O*-benzyl-2-*O*-{4-*O*-[4-*O*-(2,4-di-*O*-acetyl-3-*O*-methyl-α,β-L-xylopyranosyl)-2,3-*O*-isopropylidene-α-*L*-rhamnopyranosyl]-2,3-*O*-isopropylidene-α-*L*-rhamnopyranosyl}-α-*L*-rhamnopyranoside* (**7**). — A solution of **5** (0.50 g, 0.62 mmol) and $Hg(CN)_2$ (0.75 g, 3 mmol) in 1:1 benzene–nitromethane (60 mL) was concentrated to half volume at atmospheric pressure. The cold solution was treated with **6** (578 mg, 1.86 mmol). After 1 h, **5** had disappeared (t.l.c.) and the mixture was worked-up. Column chromatography (light petroleum–ethyl acetate, 6:4) of the product gave chromatographically homogeneous, syrupy **7** (440 mg, 68.5%), R_F 0.65. The ^{13}C-n.m.r. spectrum contained signals for anomeric carbons (95.7 and 100.2) and Me (58.7 and 58.6) of the xylopyranosyl group, showing that the newly

formed interglycosidic bond was $\alpha\beta$. These anomers could not be separated from each other.

Benzyl 4-O-(2,4-di-O-acetyl-3-O-methyl-α-L-xylopyranosyl)-2,3-O-isopropylidene-α-L-rhamnopyranoside (**8**) *and benzyl 4-O-(2,4-di-O-acetyl-3-O-methyl-β-L-xylopyranosyl)-2,3-O-isopropylidene-α-L-rhamnopyranoside* (**9**). — Benzyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside[9] (3.24 g, 11 mmol) was glycosylated with **6** (2.49 g, 8 mmol) in the presence of $Hg(CN)_2$ (2.77 g, 11 mmol) in benzene–nitromethane solution (100 mL) as described for the preparation of **7**. The reaction was complete after 15 min, and t.l.c. then revealed two disaccharide derivatives. The β anomer **9** (2.07 g, 49.3%), crystallised from ethanol, had m.p. 117–118°, $[\alpha]_D$ +1.1° (*c* 0.7, chloroform), R_F 0.52 (light petroleum–ethyl acetate, 6:4).

Anal. Calc. for $C_{26}H_{36}O_{11}$: C, 59.53; H, 6.92. Found: C, 59.81; H, 7.01.

The α anomer **8** (0.15 g, 3.6%) was obtained as a syrup by fractionation of the components in the mother liquor and had $[\alpha]_D$ −79° (*c* 1.45, chloroform), R_F 0.66.

Anal. Found: C, 59.47; H, 6.79.

Benzyl 2,3-di-O-acetyl-4-O-(2,4-di-O-acetyl-3-O-methyl-α-L-xylopyranosyl)-α-L-rhamnopyranoside (**10**). — A solution of **8** (120 mg, 0.23 mmol) in 1:1 acetic acid–water (2 mL) was kept at 80° for 30 min and then concentrated. Toluene (3 × 5 mL) was distilled from the residue which was acetylated with pyridine (1 mL) and acetic anhydride (1 mL) for 16 h. Conventional work-up then gave syrupy **10** (122 mg, 93.8%), $[\alpha]_D$ −68.5° (*c* 0.8, chloroform), R_F 0.72 (dichloromethane–acetone, 9:1).

Anal. Calc. for $C_{27}H_{36}O_{13}$: C, 57.03; H, 6.38. Found: C, 57.35; H, 6.48.

Benzyl 2,3-di-O-acetyl-4-O-(2,4-di-O-acetyl-3-O-methyl-β-L-xylopyranosyl)-α-L-rhamnopyranoside (**11**). — Compound **9** (1.64 g, 3.1 mmol) was hydrolysed with 1:1 acetic acid–water (20 mL) as described for **10**. The product was acetylated with pyridine (10 mL) and acetic anhydride (10 mL) to give **11** (1.57 g, 88.4%), m.p. 120° (from cyclohexane), $[\alpha]_D$ −11° (*c* 0.5, chloroform), R_F 0.70 (dichloromethane–acetone, 9:1).

Anal. Calc. for $C_{27}H_{36}O_{13}$: C, 57.03; H, 6.38. Found: C, 57.21; H, 6.42.

Benzyl 4-O-(3-O-methyl-α-L-xylopyranosyl)-α-L-rhamnopyranoside (**12**). — Compound **10** (85 mg, 0.15 mmol) was deacetylated with NaOMe (2 mg) in methanol (5 mL). After 24 h, the solution was neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated to give **12** as a foam (45 mg, 75.0%), $[\alpha]_D$ −92° (*c* 0.5, water).

Anal. Calc. for $C_{19}H_{28}O_9$: C, 56.98; H, 7.05. Found: C, 57.08; H, 6.99.

Benzyl 4-O-(3-O-methyl-β-L-xylopyranosyl)-α-L-rhamnopyranoside (**13**). — Compound **11** (568 mg, 1 mmol) was deacetylated in methanol (20 mL) in the presence of NaOMe (5 mg) to give **13** as a foam (350 mg, 87.5%), $[\alpha]_D$ +6° (*c* 1, water).

Anal. Calc. for $C_{19}H_{28}O_9$: C, 56.98; H, 7.05. Found: C, 56.78; H, 7.01.

2,3-Di-O-acetyl-4-O-(2,4-di-O-acetyl-3-O-methyl-β-L-xylopyranosyl)-α-L-

rhamnopyranosyl bromide (**14**). — A solution of **11** (1.8 g, 3.17 mmol) in ethanol (100 mL) and acetic acid (1 mL) was hydrogenolysed in the presence of 10% Pd/C (700 mg). After 24 h, the catalyst was removed, the filtrate was concentrated, and the residue was treated with acetic anhydride (8 mL) in pyridine (8 mL). T.l.c. (dichloromethane–acetone, 9:1) revealed two anomers (R_F 0.62 and 0.54) in the ratio ~95:5. The usual work-up gave a syrupy product (1.4 g, 85%).

A solution of a portion (380 mg, 0.75 mmol) of the above product in dry dichloromethane (3 mL) at −10° was treated with acetic acid–HBr (1.5 mL) for 15 min, then diluted with dichloromethane, washed with ice–water until neutral, dried, and concentrated to give syrupy **14** (360 mg, 88.9%), $[\alpha]_D$ −98° (*c* 0.15, chloroform), R_F 0.60 (dichloromethane–acetone, 95:5).

*Benzyl 3,4-di-*O*-benzyl-2-*O*-{4-*O*-[2,3-di-*O*-acetyl-4-*O*-(2,4-di-*O*-acetyl-3-*O*-methyl-β-*L*-xylopyranosyl)-α-*L*-rhamnopyranosyl]-2,3-*O*-isopropylidene-α-*L*-rhamnopyranosyl}-α-*L*-rhamnopyranoside* (**15**). — Compounds **3** (620 mg, 1 mmol) and **14** (360 mg, 0.66 mmol) were reacted in 1:1 benzene–nitromethane (10 mL) in the presence of $Hg(CN)_2$ (252 mg, 1 mmol). After 1 h, **14** had disappeared and the mixture was worked-up. Column chromatography (dichloromethane–acetone, 95:5) of the product gave **15** (280 mg, 38.9%) as a foam, $[\alpha]_D$ −29° (*c* 0.5, chloroform), R_F 0.64. ^{13}C-N.m.r. data ($CDCl_3$): δ 109.1 (CMe_2), 100.7, 98.5, 97.7, and 95.7 (anomeric carbons), 58.5 (OCH_3), 27.7 and 26.3 (CMe_2), 17.9, 17.6, and 17.5 (Me of rhamnopyranoside residues).

Anal. Calc. for $C_{56}H_{72}O_{21}$: C, 62.20; H, 6.66. Found: C, 62.40; H, 6.80.

*1,3,4-Tri-*O*-acetyl-2-*O*-{2,3-di-*O*-acetyl-4-*O*-[2,3-di-*O*-acetyl-4-*O*-(2,4-di-*O*-acetyl-3-*O*-methyl-β-*L*-xylopyranosyl)-α-*L*-rhamnopyranosyl]-α-*L*-rhamnopyranosyl}-α-*L*-rhamnopyranose* (**16**). — A solution of **15** (238 mg, 0.22 mmol) in 1:1 acetic acid–water (2 mL) was kept at 80° for 30 min, then diluted with ethanol (30 mL), and hydrogenolysed in the presence of Pd/C (50 mg). After 24 h, only one product could be detected (t.l.c.); this did not show any u.v. absorbtion. The catalyst was removed, the filtrate was concentrated, and toluene was distilled from residue. The resulting dry foam was conventionally acetylated with pyridine (2 mL) and acetic anhydride (2 mL). Column chromatography (dichloromethane–acetone, 9:1) of the syrupy product gave amorphous **16** (160 mg, 74.1%), $[\alpha]_D$ −168° (*c* 0.4, chloroform), R_F 0.62. The ^{1}H- and ^{13}C-n.m.r. data are recorded in Tables I and II.

Anal. Calc. for $C_{42}H_{60}O_{26}$: C, 51.42; H, 6.16. Found: C, 51.27; H, 6.28.

O-(3-O-Methyl-β-L-xylopyranosyl)-(1→4)-O-α-L-rhamnopyranosyl-(1→4)-O-α-L-rhamnopyranosyl-(1→2)-L-rhamnopyranose (**17**). — Compound **16** (123 mg, 0.125 mmol) was deacetylated in methanol (20 mL) containing NaOMe (5 mg). After 14 h, the solution was neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated to give amorphous **17** (71 mg, 94.2%), $[\alpha]_D$ −22°→ −18° (*c* 0.5, water). The ^{13}C-n.m.r. spectrum showed 24 well-separated lines (see Table I).

Anal. Calc. for $C_{24}H_{42}O_{17}$: C, 47.83; H, 7.02. Found: C, 48.06; H, 7.09.

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