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A NEW METHOD OF OLIGOSACCHARIDE SYNTHESIS: RHAMNOTRIOSES

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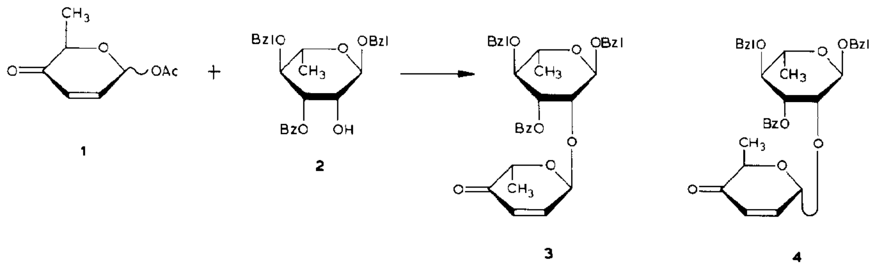
ABSTRACT

Condensation of partially protected rhamnobiose derivatives with 1-*O*-acetyl-2,3,6-trideoxy-α,β-DL-*glycero*-hex-2-enopyranos-4-ulose afforded pairs of diastereoisomeric α-linked trisaccharide derivatives to which the configuration was assigned on the basis of spectral and chemical data. Reduction of the carbonyl group in these products led to 2″,3″-unsaturated trisaccharide derivatives containing a 2,3-unsaturated α-*erythro* unit. *cis*-Hydroxylation of the double bond in five of these unsaturated compounds gave rhamnotriose derivatives, two of which were deprotected to give the trisaccharides α-L-Rha*p*-(1→2)-α-L-Rha*p*-(1→3)-L-Rha*p* and α-D-Rha*p*-(1→2)-α-L-Rha*p*-(1→3)-L-Rha*p*, respectively.

INTRODUCTION

In the previous paper[1], a new method of disaccharide synthesis was presented, exemplified by the condensation of 1-*O*-acetyl-2,3,6-trideoxy-α,β-DL-*glycero*-hex-2-enopyranos-4-ulose (**1**) with a partially protected benzyl L-rhamnopyranoside (*e.g.*, **2**), followed by separation of the resulting diastereoisomers **3** and **4**, reduction and hydroxylation of the dihydropyranone ring, and then removal of the protecting groups to give the rhamnobiose.

Monoesterification of the hydroxylation product would yield derivatives suitable for the synthesis of trisaccharides. The syntheses of five rhamnotrioses now described exemplify this strategy.



1 **2** **3** **4**

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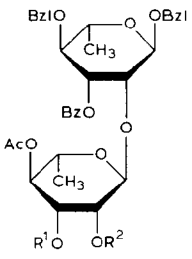
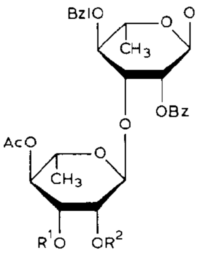
RESULTS AND DISCUSSION

Treatment of the (1→2)-α-linked rhamnobiose derivative[1] (**5**) with 1 mol of benzoyl chloride in pyridine gave the 3′-mono-, 2′-mono-, and 2′,3′-di-benzoates **6–8** in the ratios 8.3:2.5:1 (84% combined yield). Esterification of **5** with benzoic anhydride in the presence of triethylamine was less regioselective and afforded **6** and **7** in the ratio 1:1.4. Addition of a catalytic amount of 4-dimethylaminopyridine to this reaction greatly enhanced the rate of esterification, but the main product was **8** (43%); the combined yield of **6** and **7** was ~25%. Likewise, benzoylation of the (1→3)-α-linked rhamnobiose derivative[1] **9** with benzoyl chloride and pyridine afforded the 3′-mono-, 2′-mono-, and 2′,3′-di-benzoates **10–12** in yields of 62, ~9, and 21%, respectively. The location of the newly introduced benzoyl groups could be determined readily from the ^{1}H-n.m.r. spectra, where the characteristic signals for H-2′ and/or H-3′ were clearly discernible in the region δ 5.3–5.7.

Condensation of 1-*O*-acetyl-2,3,6-trideoxy-α,β-DL-*glycero*-hex-2-enopyranos-4-ulose (**1**) with benzyl 2-*O*-(4-*O*-acetyl-3-*O*-benzoyl-α-L-rhamnopyranosyl)-3-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (**6**) catalysed by stannic chloride gave four products, of which the two main compounds **13** (30%) and **16** (34%) were isolated by chromatography. The values $J_{1'',2''}$ ~3.5 and $J_{1'',3''}$ <0.5 Hz indicated the newly introduced pyranosyl group to be α and that these products were L-L-L and D-L-L diastereoisomers*. The assignment of configurations to **13** and **16** was also possible on the basis of the chemical shifts of the ^{1}H signals of Me-5, Me-5′, and Me-5″, namely, for **13**, at δ 1.34, 1.04, and 0.97, and for **16**, at δ 1.40, 1.06, and 0.67. The high-field position of the signal for Me-5″ in **16** is due[1] to the anisotropic shielding effect of an aromatic ring and is characteristic for the D configuration of the new unit.



5 $R^1 = R^2 = H$
6 $R^1 = Bz, R^2 = H$
7 $R^1 = H, R^2 = Bz$
8 $R^1 = R^2 = Bz$



9 $R^1 = R^2 = H$
10 $R^1 = Bz, R^2 = H$
11 $R^1 = H, R^2 = Bz$
12 $R^1 = R^2 = Bz$

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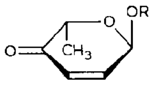
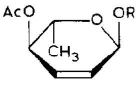
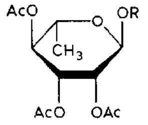
*The designations L-L-L and D-L-L denote the configurations of the units of the trisaccharides and their derivatives, starting from the non-reducing end.



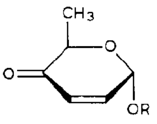
13–15



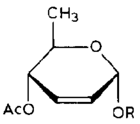
19–21



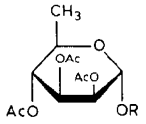
25–27



16–18



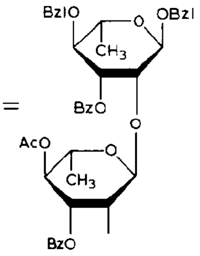
22–24



28–29

13,16,19,22,25,28 : R = A
14,17,20,23,26 : R = B
15,18,21,24,27,29 : R = C

A =



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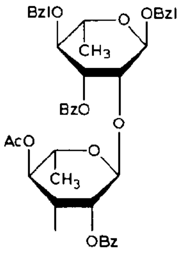

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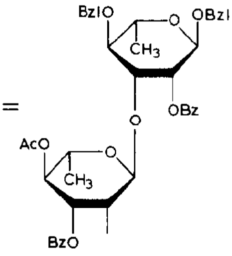


The other two products of condensation of **1** and **6** were formed in minute quantities and were not isolated but, on the basis of previous experience[1], they were most probably the corresponding β-linked derivatives.

Likewise, condensation of **1** and benzyl 3-*O*-(4-*O*-acetyl-3-*O*-benzoyl-α-L-rhamnopyranosyl)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (**10**) gave the α-linked trisaccharide derivatives **15** (30%) and **18** (35%), and their L-L-L and D-L-L configurations, respectively, were indicated by the ^{1}H signals for Me-5, Me-5′, and Me-5″, occurring at δ 1.34, 1.19, and 1.07 for **15**, and at δ 1.38, 1.11, and 0.60 for **18**.

Such a configurational assignment was not possible for the products of condensation of **1** and benzyl 2-*O*-(4-*O*-acetyl-2-*O*-benzoyl-α-L-rhamnosyl)-3-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (**7**), namely, **14** (33%) and **17** (28%), which were shown to contain only α linkages. However, following condensation of (+)-D-**1**[1] with **7**, it was possible to assign the D-L-L configuration to the less-polar product **17**, so that **14** must have been L-L-L.

Physical and analytical data for **13**–**18** are recorded in Table I.

Reduction of the carbonyl group in **13** gave a single product in good yield, which was characterised as the 4″-acetate **19**. The configuration of the unsaturated unit in **19** could not be determined from the 100-MHz ^{1}H-n.m.r. data, but earlier

TABLE I

DATA FOR COMPOUNDS **13–31**

Compound	*Yield (%)*	*M.p. (degrees)*	$[\alpha]^{18}_{D}$ *(deg) (c, chloroform)*	*Formula*	*Elemental analysis*			
					Calc.		*Found*	
					C	*H*	*C*	*H*
13	30.1[a]	56–58	+30.3 (0.8)	$C_{48}H_{50}O_{14} \cdot 2\,H_2O$	65.00	6.14	65.30	6.14
14	33.1[b]	[c]	+29.5 (1.05)	$C_{48}H_{50}O_{14} \cdot 2\,H_2O$	66.35	6.03	66.59	6.21
15	30.4[d]	166–168	+11.7 (0.35)	$C_{48}H_{50}O_{14}$	67.75	5.92	67.72	6.03
16	34.2[a]	57–58	+21.5 (1.0)	$C_{48}H_{50}O_{14} \cdot 2\,H_2O$	66.35	6.03	66.53	6.06
17	28.4[b]	[c]	+7.6 (0.9)	$C_{48}H_{50}O_{14} \cdot 2\,H_2O$	66.35	6.03	66.43	6.13
18	35.1[d]	[c]	+10.1 (1.4)	$C_{50}H_{54}O_{14}$	67.75	5.92	67.61	6.00
19	67.3	[c]	−4.4 (1.1)	$C_{50}H_{54}O_{15}$	67.10	6.08	66.75	6.36
20	93.5	[c]	+7.3 (0.9)	$C_{50}H_{54}O_{15}$	67.10	6.08	66.98	6.43
21	80.0	[c]	−10.8 (1.7)	$C_{50}H_{54}O_{15}$	67.10	6.08	66.86	6.06
22	99.0	[c]	+37.4 (0.7)	$C_{50}H_{54}O_{15}$	67.10	6.08	66.67	6.37
23	86.5	[c]	+42.3 (0.5)	$C_{50}H_{54}O_{15}$	67.10	6.08	67.18	6.31
24	79.6	[c]	+26.9 (1.2)	$C_{50}H_{54}O_{15}$	67.10	6.08	66.85	6.16
25	72.4	[c]	−7.1 (0.45)	$C_{54}H_{60}O_{19}$	64.02	5.97	63.86	5.98
26	65.0	[c]	~0 (0.4)	$C_{54}H_{60}O_{19}$	64.02	5.97	63.52	5.97
27	91.1	[c]	−10.0 (0.6)	$C_{54}H_{60}O_{19}$	64.02	5.97	63.74	6.01
28	75	[c]	+42.2 (0.4)	$C_{54}H_{60}O_{19}$	64.02	5.97	63.56	6.00
29	83.9	[c]	+37.4 (0.3)	$C_{54}H_{60}O_{19}$	64.02	5.97	63.92	5.98
30	87	[c]	−40.9 (0.5)[e]	$C_{18}H_{32}O_{13}$	47.36	7.07	46.98	7.03
31	77.3	110–112	+2.8 (0.85)[e]	$C_{18}H_{32}O_{13}$	47.36	7.07	47.22	7.39

[a] A third fraction (<5%) containing two products (t.l.c.) was isolated, but not analysed further. [b] Of the substrate **7**, ~19% was recovered after chromatography. [c] Amorphous solid. [d] A third fraction (16.1%) containing several products was obtained after chromatographic separation of **15** and **18**, but this fraction was not analysed further. [e] Recorded in methanol.

evidence[1] strongly suggested the *erythro* configuration. Support for this assignment was provided by the chemical shifts of the AcO signals at δ 2.00 and 1.96. According to Lichtenthaler and Emig[2], the protons of equatorial (and also pseudoequatorial) acetyl groups resonate at δ 1.97–2.12, and those of axial groups at δ 2.10–2.25. On this basis, the acetyl groups of **19** are pseudoequatorial and the configuration of the unsaturated moiety is *α-erythro*.

Similar results were obtained on reduction of the five trisaccharide derivatives **14–18**. Each product was isolated and characterised as the 4″-acetate. The yields and physical and analytical data for **19–24** are collected in Table I.

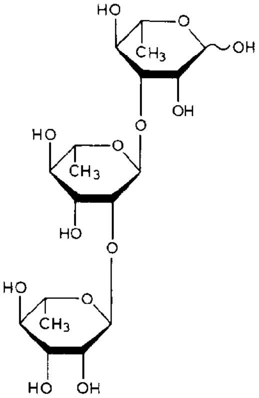
Each of the unsaturated compounds **19–24** (with the exception of **23**) was *cis*-hydroxylated with osmium tetraoxide in pyridine. It is well known[1,5] that, in this reaction, the hydroxyl groups are introduced *trans* to substituents at C-1″ and C-4″, resulting in generation of the rhamnose structure. Acetylation of the products gave the trisaccharide derivatives **25–29** in good yields (Table I). Removal of the protecting groups from **27** and **29** gave *α*-L-Rha*p*-(1→2)-*α*-L-Rha*p*-(1→3)-L-Rha*p* (**30**) and *α*-D-Rha*p*-(1→2)-*α*-L-Rha*p*-(1→3)-L-Rha*p* (**31**), respectively.

TABLE II

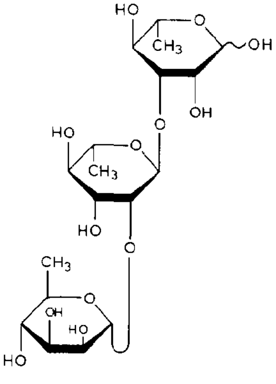
^{13}C-N M.R DATA FOR RHAMNOTRIOSES **25**, **26**, **28**, **30**, AND **31**

Atom	**25**[a]	**26**[a]	**28**[a]	**30**[b]	**31**[b]
C-1″	100.6	98.9	94.8	103.0	99.1
C-2″	69.6	70.1	68.2	71.5	71.5
C-3″	68.9	68.8	68.8	70.8	70.9
C-4″	71.1	70.8	69.6	72.9	72.8
C-5″	67.1	67.4	66.8	69.9	70.2
C-6″	17.2	17.2	17.3	17.4	17.4
C-1′	99.1	98.6	99.3	101.6	100.0
C-2′	78.1	72.0	71.5	77.9	75.9
C-3′	71.7	76.1	71.9	70.8	71.2
C-4′	71.1	71.5	71.3	72.8	72.8
C-5′	67.1	67.2	67.5	69.9	69.7
C-6′	17.2	17.3	17.5	17.4	17.6
C-1	97.5	97.5	97.5	94.7	94.6
C-2	76.6	76.2	76.3	72.0	72.0
C-3	73.6	73.4	73.4	78.9	78.8
C-4	79.2	79.3	79.2	72.8	72.7
C-5	68.0	68.3	68.2	69.1	69.3
C-6	18.1	18.1	18.1	17.4	17.4
Benzyl					
CH_2-1	69.1	69.1	69.0		
CH_2-4	75.2	75.1	75.2		

[a] In deuteriochloroform (internal Me_4Si). [b] In D_2O [internal 1,4-dioxane; δ (Me_4Si) 67.35].



30



31

The ^{13}C-n.m.r. data for the trisaccharide derivatives **25**, **26**, and **28**, and of the rhamnotrioses **30** and **31** are recorded in Table II. The assignment of signals was made by analogy with the assignments for rhamnobioses[1] and rhamnotrioses[3]. The α-shifts associated with the signals of the D-rhamnose residues are remarkably low compared with those of L-rhamnose[1].

In solution in methanol, the rhamnotrioses **30** and **31** exist as $\alpha\beta$-mixtures with ratios of 1.3:1 for **30**, and 1.7:1 for **31**, as indicated by the intensity of the signal for C-1β at δ 94.2.

Of the five rhamnotrioses described in the present work, α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→2)-L-Rha*p* is known[3], and the 8-methoxycarbonyloctyl glycoside of α-L-Rha*p*-(1→2)-α-L-Rha*p*-(1→3)-L-Rha*p* has been described[4]. The synthesis strategy described above should be adaptable for the synthesis of tetrasaccharides. However, the difficulties associated with separation of diastereoisomeric products of condensation and the problem of configuration assignment indicate that a pure enantiomer of the enulose acetate of known absolute configuration should be used.

EXPERIMENTAL

General methods. — N.m.r. spectra were recorded with Jeol JNM-4H-100 (100 MHz, ^{1}H) and 90-Q (^{13}C) spectrometers. I.r. spectra were recorded with Unicam SP-200 and Beckman IR 4240 spectrophotometers. Optical rotations were measured with a Perkin–Elmer 141 automatic polarimeter at 18 ±1°. For column chromatography, MN silica gel (<0.08) and Merck silica gel 60 (230–400 mesh) were used.

Benzyl 2-*O*-(4-*O*-acetyl-α-L-rhamnopyranosyl)-3-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (**5**), benzyl 3-*O*-(4-*O*-acetyl-α-L-rhamnopyranosyl)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (**9**), and 1-*O*-acetyl-2,3,6-trideoxy-α,β-DL-*glycero*-hex-2-enopyranos-4-ulose[6] (**1**) were obtained as previously described. Acetylations were performed conventionally with acetic anhydride and pyridine at room temperature.

Benzyl 2-O-(4-O-acetyl-3-O-, -2-O-, and -2,3-di-O-benzoyl-α-L-rhamnopyranosyl)-3-O-benzoyl-4-O-benzyl-α-L-rhamnopyranoside (**6–8**). — (*a*) To a solution of **5**[1] (2.1 g) in 2:1 benzene–pyridine (18 mL) at 0° was added benzoyl chloride (0.62 mL), and the mixture was stirred for 1 h at 0° and then allowed to attain room temperature during 1 h. The mixture was poured into ice–water and extracted with chloroform, and the extract was washed with cold aqueous 3% hydrochloric acid and water, dried, and concentrated. The residue was subjected to flash chromatography with 4:1 light petroleum–ethyl acetate, to give, first, amorphous **8** (0.174 g, 7.1%), $[\alpha]_D$ +24° (*c* 0.65, chloroform); ν_{max}^{KBr} 1690, 1610, 1460, 1430, 1295, 1130, 1075, 1030, and 700 cm^{-1}.

Anal. Calc. for $C_{49}H_{48}O_{13}$: C, 69.65; H, 5.73. Found: C, 69.78; H, 5.70.

Eluted second was amorphous **6** (1.44 g, 59.0%), $[\alpha]_D$ +14° (*c* 1.15, chloroform); ν_{max}^{KBr} 3510, 1720, 1600, 1460, 1275, 1230, 1105, 1065, 1040, 1020, 740, 730, 700, and 695 cm^{-1}.

Anal. Calc. for $C_{42}H_{44}O_{12}$: C, 68.09; H, 5.99. Found: C, 68.01; H, 6.06.

Eluted third was amorphous **7** (0.433 g, 17.7%), $[\alpha]_D$ +2° (*c* 1.2, chloroform); ν_{max}^{KBr} 3500, 1720, 1600, 1460, 1265, 1100, 1090, 1070, 1040, 1020, 740, 730, 700, and 695 cm^{-1}.

Anal. Calc. for $C_{42}H_{44}O_{12}$: C, 68.09; H, 5.99. Found: C, 68.25; H, 6.34.

(*b*) Treatment of a solution of **5** (0.764 g) in dichloromethane (5 mL) with benzoic anhydride (0.42 g) and triethylamine (0.3 mL) for 3 days at room temperature gave, after work-up and chromatography, **6** (0.225 g, 25.3%), **7** (0.316 g, 35.7%), and **5** (0.367 g).

Addition of a few crystals of 4-dimethylaminopyridine to the foregoing reaction mixture reduced the time of esterification to 1 day, but the yields of **6–8** were 12, 13, and 43%, respectively.

*Benzyl 3-O-(4-O-acetyl-3-O-, -2-O-, and -2,3-di-O-benzoyl-α-*L*-rhamnopyranosyl)-2-O-benzoyl-4-O-benzyl-α-*L*-rhamnopyranoside* (**10–12**). — Treatment of **9**[1] (2.06 g) with benzoyl chloride and pyridine, as described for **5**, and chromatography of the product with 4:1 light petroleum–ethyl acetate gave, first, **12** (0.5 g, 20.8%), as a syrup, $[\alpha]_D$ +44° (*c* 0.4, chloroform); ν_{max}^{film} 1745, 1610, 1500, 1460, 1270, 1230, 1115, 1100, 1070, 1030, and 710 cm^{-1}.

Anal. Calc. for $C_{49}H_{48}O_{13}$: C, 69.65; H, 5.73. Found: C, 69.72; H, 5.91.

Eluted second was amorphous **10** (1.483 g, 61.8%), $[\alpha]_D$ ~0° (*c* 0.4, chloroform); ν_{max}^{Nujol} 3450, 1730, 1600, 1460, 1275, 1240, 1230, 1150, 1075, 1060, 1030, 760, 745, and 710 cm^{-1}.

Anal. Calc. for $C_{42}H_{44}O_{12}$: C, 68.09; H, 5.99. Found: C, 67.88; H, 5.99.

Eluted third was an impure substance (0.22 g, 9.2%) which was probably the monobenzoate **11**. This fraction was not investigated further.

*Condensation of rhamnobiose derivatives with 1-O-acetyl-2,3,6-trideoxy-α,β-*DL-glycero-*hex-2-enopyranos-4-ulose* (**1**). — In view of the similarity of the procedures used for condensation of the rhamnobiose derivatives with **1**, reduction of the carbonyl group in the products, and *cis*-hydroxylation, only general descriptions are given below.

A solution of **6**, **7**, or **10** (740 mg, 1 mmol) and **1** (225 mg, 1.3 mmol) in 1,2-dichloroethane (10 mL) was treated with M stannic chloride in dichloromethane (0.25 mL). After 20 h at room temperature, each mixture was diluted with dichloromethane (40 mL), immediately washed with dilute, aqueous sodium hydrogencarbonate and water, dried ($MgSO_4$), and concentrated. Each residue was subjected to flash chromatography[7] with 70:30:1 light petroleum–ether–methanol. The products **13–18** were isolated in a pure state. Their physical and analytical data are collected in Table I, and the ^{1}H-n.m.r. data in Table III.

To solutions of sodium borohydride (0.22 g, 5.8 mmol) in 4:1 tetrahydrofuran–water (5 mL) were added solutions of the trisaccharide derivatives **13–18** (250 mg, 3 mmol) in tetrahydrofuran (0.5 mL), and each mixture was stirred at room temperature. After completion of the reaction (1.5–2 h; t.l.c.), each mixture was diluted with water (~20 mL) and extracted with ether, and the extract was dried ($MgSO_4$) and concentrated. Each residue was acetylated and the product was purified by chromatography on a column of silica gel with 7:3 light petroleum–ethyl acetate. The physical and analytical data for the products **19–21**, **23**, and **24** are recorded in Table I, and the ^{1}H-n.m.r. data in Table III.

TABLE III

^{1}H-N.M.R. DATA FOR COMPOUNDS **6–8**, **10** AND **12–29**[a]

Compound	*Unit*	*Chemical shifts (δ)*							*Coupling constants (Hz, first order)*				
		H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*Acetyl*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$
6	N[b]	4.92	4.27[c]	5.61[d]	5.29	3.92	1.07	1.94	—	3.5	9.0	9.5	6.2
	R[b]	4.87	4.17[c]	5.45[d]	3.77	3.92	1.37		—	3.5	9.0	9.5	6.0
7	N	5.03	5.54	4.20	4.95	3.86	1.07	2.12	—	3.5	—	—	6.0
	R	4.83	4.17	5.69	3.73	3.86	1.36		—	3.5	9.0	9.5	6.0
8	N	5.03	5.86	5.75	5.34	4.0	1.13	1.96	—	3.5	9.5	9.5	6.0
	R	4.90	4.20	5.75	3.83	4.0	1.40		—	3.5	9.0	9.0	6.0
10	N	5.09	4.15	5.30	5.21	3.85	1.07	1.79	—	—	—	—	6.0
	R	5.01	5.44	4.29	3.68	3.85	1.35		—	3.5	9.5	9.5	6.0
12	N	5.02	5.48	5.66	5.33	3.86	1.06	1.84	—	3.5	—	—	6.0
	R	4.80	5.48	4.37	3.70	3.86	1.35		—	3.5	9.5	9.5	6.0
13	N″	4.89	6.63	5.97	—	4.33	0.94	1.98	3.5	10.0	—	—	6.5 $J_{1,3}$ <0.5
	N′	4.89	4.28	5.57[c]	5.23	3.90	1.04		—	3.5	9.0	9.5	6.0
	R	4.89	4.28	5.49[c]	3.77	3.90	1.38		—	3.5	9.0	9.5	6.0
14	N″	5.35	6.61	6.00	—	4.50	1.07	2.10	3.5	10.3	—	—	6.5 $J_{1,3}$ <0.5
	N′	5.04	5.6–5.8	4.32	5.17	3.91	1.18		—	3.5	9.5	9.5	6.0
	R	4.85	4.19	5.6–5.8	3.76	3.91	1.35		1.75	3.5	9.5	9.5	6.0
15	N″	5.33	6.68	6.01	—	4.50	1.07	1.81	3.5	10.0	—	—	6.5 $J_{1,3}$ <0.5
	N′	5.18	4.26	5.1——5.4		3.85	1.19		—	3.5	—	—	6.0
	R	5.06	5.43	4.29	3.66	3.85	1.34		—	3.5	9.5	9.5	6.0
16	N″	5.1–5.4	6.42	5.95	—	4.31	0.67	1.97	3.5	10.0	—	—	6.5 $J_{1,3}$<0.5
	N′	4.85	4.26	5.61[c]	5.21	3.96	1.06		—	3.5	9.0	9.5	6.2
	R	4.75	4.26	5.47[c]	3.79	3.96	1.40		—	3.5	9.0	9.5	6.0
17	N″	5.47	6.65	5.95	—	4.4–4.6	1.08	2.02	3.5	10.0	—	—	6.2 $J_{1,3}$<0.5
	N′	4.97	5.75	4.38	5.06	3.92	1.39		—	3.5	9.5	9.5	6.0
	R	4.86	4.19	5.68	3.84	3.92	1.41		—	3.5	9.5	9.5	6.0
18	N″	5.0–5.3	6.52	5.94	—	4.2–4.5	0.60	1.84	3.5	10.0	—	—	6.5 $J_{1,3}$<0.5
	N″	5.0–5.3	4.2–4.5	5.1——5.3		3.89	1.11		—	—	—	—	6.0
	R	5.0–5.3	5.46	4.2–4.5	3.67	3.89	1.38		—	—	9.5	9.5	6.0

	N″	4.87	5.71	5.71	5.34	3.99	0.76	2.00	—	—	9.0	9.0	6.2
19	N′	4.87	4.21	5.59[c]	5.26	3.99	1.05	1.96	—	3.2	9.5	9.5	6.0
	R	4.87	4.21	5.50[c]	3.88	3.99	1.40		—	3.0	9.5	9.5	6.0
	N″	5.13[c]	5.4—	—5.9	4.8	3.88	1.06	1.99	—	—	—	—	6.2
20	N′	5.02[c]	5.4–5.9	4.23	5.13	3.88	1.18	1.91	—	3.5	—	—	6.0
	R	4.83	4.16	5.4–5.9	3.74	3.88	1.35		—	3.5	9.5	9.5	6.0
	N″	5.13	5.77	5.77	4.8–5.0	3.88	1.07	2.06	—	—	—	—	6.0
21	N′	5.0	4.23	5.32	4.8–5.0	3.88	1.07	1.77	—	—	—	—	6.0
	R	5.0	5.44	4.27	3.66	3.88	1.33		—	3.5	9.5	9.5	6.0
	N″	4.7–4.9	5.1—	—	—5.8	3.93	0.57	2.01	—	—	—	—	6.5
22	N′	4.7–4.9	4.22	5.1–5.8	5.1–5.8	3.93	1.06	1.95	—	—	9.5	9.5	6.0
	R	4.7–4.9	4.22	5.1–5.8	3.81	3.93	1.38		—	—	9.5	9.5	6.0
	N″	4.9–5.2	5.4—	—6.0	4.9–5.2	3.88	1.06	2.08	—	—	—	—	6.0
23	N′	4.9–5.2	5.4–6.0	4.32	4.9–5.2	3.88	1.26	1.98	—	3.5	9.5	—	6.0
	R′	4.9–5.2	4.17	5.4–6.0	3.73	3.88	1.37		—	—	9.5	9.5	6.0
	N″	4.9–5.1	5.68	5.68	4.9–5.1	3.84	0.50	1.96	—	—	—	—	6.0
24	N′	4.9–5.1	4.38[c]	5.1–5.4	5.1	3.84	1.10	1.82	—	—	—	—	6.0
	R	4.89	5.44	4.30[c]	3.68	3.84	1.37		—	—	9.5	9.5	6.0
	N″	4.6–4.9	5.1—	—	—5.3	3.8–4.0	0.82	2.06	—	—	—	—	6.0
25	N′	4.6–4.9	4.15[c]	5.55	5.1–5.3	3.8–4.0	1.08	2.00 1.99	—	—	—	—	6.0
	R	4.6–4.9	4.23[c]	5.55	3.76	3.8–4.0	1.37	1.86	—	—	—	—	6.0
	N″	4.5–5.2	4.6—	—	—5.2	3.87	1.07	2.20 2.18	—	—	—	—	6.0
26	N′	4.5–5.2	5.0–5.7	4.15	4.6–5.2	3.87	1.14	1.98	—	—	—	—	6.0
	R	4.5–5.2	4.15	5.0–5.7	3.72	3.87	1.44	1.96	—	—	—	—	6.0
	N″	5.11	5.1—	—	—5.5	3.84	1.07	2.04 1.99	—	—	—	—	6.0
27	N′	5.02	4.04	5.1–5.5	5.1–5.5	3.84	1.07	1.96	—	—	—	—	6.0
	R	4.92	5.1–5.5	4.25	3.65	3.84	1.32	1.77	—	3.5	9.5	9.5	6.0
	N″	4.6–5.3	4.6—	—	—5.3	3.90	1.15	2.17 2.12	—	—	—	—	6.0
28	N′	4.6–5.3	5.69	4.22	4.6–5.3	3.90	1.33	1.99	—	3.5	—	—	6.0
	R	4.6–5.3	4.18	5.69	3.74	3.90	1.45	1.92	—	—	9.5	9.5	6.0
	N″	4.7–5.3	4.7—	—	—5.3	3.80	0.57	2.05 1.95	—	—	—	—	6.0
29	N′	4.7–5.3	4.29	5.27	4.7–5.3	3.80	1.02	1.86	—	—	—	—	6.0
	R	4.7–5.3	5.43	4.29	3.64	3.80	1.34	1.82	—	3.5	9.5	9.5	6.0

[a] Signals of benzyl and benzoyl protons are omitted. [b] N″, N′, N, non-reducing units; R, reducing unit. [c,d] The assignments may be reversed.

A solution of each of the unsaturated derivatives **19–21**, **23**, and **24** in pyridine (268 mg, 0.3 mmol) was treated with a solution of osmium tetraoxide (300 mg) in pyridine (1.2 mL). After stirring for 3 days at room temperature, sodium hydrogensulfite (0.6 g), pyridine (6 mL), and water (9 mL) were added and stirring was continued for 2 days. Each mixture was then diluted with water (50 mL) and extracted with dichloromethane, and the extract was washed with water, dried, and concentrated. Each syrupy residue was purified by chromatography with 2:1 light petroleum–ethyl acetate, and the product was acetylated. Yields and physical and analytical data for the products **25–28** are recorded in Table I, and the ^{1}H-n.m.r. data in Table III.

α-L-Rhap-(1→2)-α-L-Rhap-(1→3)-L-Rhap (**30**). — To a solution of **27** (0.239 g) in dry methanol (15 mL) was added sodium (~100 mg). After 12 h at room temperature, the mixture was neutralised with Amberlite IR-120 (H$^+$) resin and concentrated. A solution of the residue in ethanol (20 mL) was shaken in a hydrogen atmosphere for 9 h in the presence of 10% Pd/C (100 mg), filtered, and concentrated, to give amorphous **30** (96 mg, 87%).

Using an analogous procedure, **29** (218 mg) was converted into α-D-Rha*p*-(1→2)-α-L-Rha*p*-(1→3)-L-Rha*p* (**31**; 76 mg, 77.3%).

Physical and analytical data for **30** and **31** are collected in Table I, and the ^{13}C-n.m.r. data in Table II.

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