Carbohydrate Research, 90 (1981) 215–231
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

SYNTHESIS, AND CARBON-13 N M R STUDY, OF *O*-α-L-RHAMNOPYRANOSYL-(1→3)-*O*-α-L-RHAMNOPYRANOSYL-(1→2)-L-RHAMNOPYRANOSE AND *O*-α-L-RHAMNOPYRANOSYL-(1→3)-*O*-α-L-RHAMNOPYRANOSYL-(1→3)-L-RHAMNOPYRANOSE, CONSTITUENTS OF BACTERIAL, CELL-WALL POLYSACCHARIDES*

VINCE POZSGAY,
Biogal Pharmaceutical Works, Debrecen, H-4042 (Hungary)

PAL NANASI,
Institute of Biochemistry, L Kossuth University, Debrecen, H-4010 (Hungary)

AND ANDRAS NESZMELYI
Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest Pusztaszeri ut, H-1525 (Hungary)

(Received September 16th, 1980 accepted for publication, November 4th 1980)

ABSTRACT

O-α-L-Rhamnopyranosyl-(1→3)-L-rhamnopyranose (**19**) and *O*-α-L-rhamnopyranosyl-(1→2)-L-rhamnopyranose were obtained by reaction of benzyl 2,4- (**7**) and 3,4-di-*O*-benzyl-α-L-rhamnopyranoside (**8**) with 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide, followed by deprotection The per-*O*-acetyl α-bromide (**18**) of **19** yielded, by reaction with **8** and **7**, the protected derivatives of the title trisaccharides (**25** and **23**, respectively), from which **25** and **23** were obtained by Zemplen deacetylation and catalytic hydrogenolysis, With benzyl 2,3,4-tri-*O*-benzyl-β-D-galactopyranoside, compound **18** gave an ~3 2 mixture of benzyl 2,3,4-tri-*O*-benzyl-6-*O*-[2,4-di-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl]-β-D-galactopyranoside and 4-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-L-rhamnopyranose 1,2-(1,2,3,4-tetra-*O*-benzyl-β-D-galactopyranose-6-yl (orthoacetate) The downfield shift at the α-carbon atom induced by α-L-rhamnopyranosylation at HO-2 or -3 of a free α-L-rhamnopyranose is 7 4–8 2 p p m , ~1 p p m higher than when the (reducing-end) rhamnose residue is benzyl-protected (6 6–6 9 p p m) α-L-Rhamnopyranosylation of HO-6 of β-D-galactopyranose deshields the C-6 atom by 5 7 p p m The 1,2-orthoester ring structure [$O_2C(Me)OR$] gives characteristic resonances at 24 5 ±0 2 p p m for the methyl, and at 124 0 ±0 5 p p m for the quaternary, carbon atom

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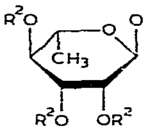
*Some of the results described in this paper were published as preliminary reports (see refs 1 and 2), and were presented (by V P) at the EUCHEM Conference on Polysaccharides from Microorganisms, Stockholm Sweden June 18–21 1979

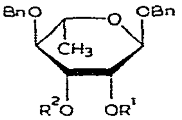
INTRODUCTION

Because of the frequent occurrence in Nature of L-rhamnose (**13**), mainly in oligo- and poly-saccharides that are constituents of immunodeterminant, bacterial capsules and lipopolysaccharides[3], and also as part of plant glycosides[4]. the synthesis of oligosaccharides containing one or more L-rhamnose units has become an attractive challenge to carbohydrate chemists

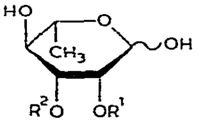
Rational synthesis of 4-*O*-glycosylrhamnoses presents no difficulties, as the HO-2 and HO-3 groups of an L-rhamnopyranoside are readily protected by an isopropylidene group[5 6], leaving only the reactive[7] HO-4 group free On the other hand, the lack, until recently, of L-rhamnose derivatives having only either HO-2 or HO-3



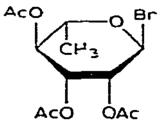
1 R^1 = Bn R^2 = H
2 R^1 = Me R^2 = H
3 R^1 = Me R^2 = Ac
4 R^1 = H R^2 = Ac
5 R^1 = R^2 = Ac
Bn = $PhCH_2$



6 R^1 = R^2 = H
7 R^1 = Bn R^2 = H
8 R^1 = H R^2 = Bn
9 R^1 = All R^2 = H
All = $H_2C{=}CHCH_2$



11 R^1 = Me R^2 = H
12 R^1 = H, R^2 = Me
13 R^1 = R^2 = H



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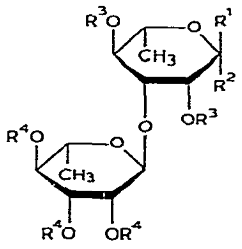
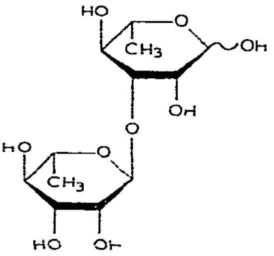


14 R^1 = OBn R^2 = H R^3 = Bn R^4 = Ac
15 R^1 = OBn R^2 = H R^3 = Bn R^4 = H
16 R^1 = OAc R^2 = H R^3 = R^4 = Ac
17 R^1 = H R^2 = OAc, R^3 = R^4 = Ac
18 R^1 = Br R^2 = H R^3 = R^4 = Ac

unsubstituted had made the synthesis of 2-*O*- and 3-*O*-glycosyl-L-rhamnoses quite laborious[7-9] In these syntheses, pioneered by King and Bishop[7,8], benzyl (**1**) or methyl α-L-rhamnopyranoside (**2**) was used as the "aglycon" moiety of the disaccharide to be built up Of the three secondary hydroxyl groups present in **1** or **2**, HO-3 and HO-4 were mainly glycosylated, and only very small proportions of 2-*O*-glycosyl-L-rhamnoses were formed The isomeric disaccharides formed had to be separated, and the structures of the individual products had to be determined In a recent synthesis[10], benzyl 4-*O*-benzyl-β-L-rhamnopyranoside was allowed to react with 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide[11] (**10**) and contrary to the order[8] of reactivity of the hydroxyl groups of **1** in glycosylation reactions, the much more preferential formation of the 2-*O*-rhamnosyl derivative was observed

The first rational synthesis of a 3-*O*-glycosyl-L-rhamnopyranoside derivative was reported by Garegg and Hultberg[12,13] Subsequently, we described[1] the synthesis of *O*-α-L-rhamnopyranosyl-(1→3)-L-rhamnopyranose (**19**) and *O*-α-L-rhamnopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→3)-L-rhamnopyranose (**23**), and also[2] of *O*-α-L-rhamnopyranosyl-(1→2)-L-rhamnopyranose (**20**) and *O*-β-D-galactopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-L-rhamnopy-



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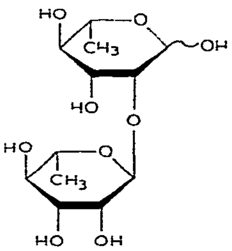

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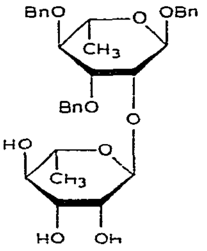

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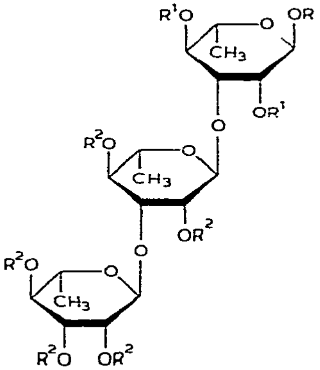
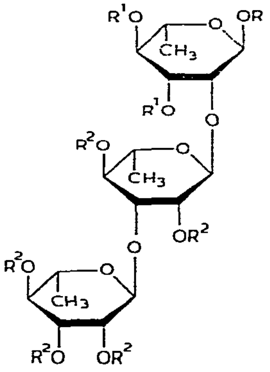


22 R^1 = Bn R^2 = Ac

23α R^1 = R^2 = H



24 R^1 = Bn R^2 = Ac

25α R^1 = R^2 = H

ranose, using benzyl 2,4- (7, ref 14) and 3,4-di-*O*-benzyl-α-L-rhamnopyranoside[14] (**8**) as the aglycon components Rational synthesis of protected derivatives of **19** and **20** was also reported in a preliminary paper[15] by using, instead of **7** and **8**, the corresponding methyl rhamnosides, and very recently, the synthesis of several 2-*O*-glycosyl-L-rhamnopyranosides by use of an α-L-rhamnopyranoside derivative having only HO-2 free has been described[16]

We now report the synthesis of **23**, which has been shown to occur in *Klebsiella* K36 capsular polysaccharide[17] and in pneumococcal type 2 capsular polysaccharide[18], and of *O*-α-L-rhamnopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-L-rhamnopyranose (**25**), a component of, *inter alia*, *Klebsiella* type 9 capsular polysaccharide[19] and *Klebsiella* O-group 7 lipopolysaccharide[20] We also discuss the ^{13}C-n m r spectra of these compounds, and those of the intermediates

RESULTS AND DISCUSSION

We have found[1,14] that benzyl 4-*O*-benzyl-α-L-rhamnopyranoside[21] (**6**) gives, under phase-transfer-catalyzed conditions[22], with a variety of reagents, the 2,4-disubstituted derivatives in 60–80% yields* Using benzyl bromide as the alkylating reagents, **7** was obtained in 70% yield after chromatography In this reaction, **8** is formed in <10% yield We have obtained **8** in a 50% overall yield from benzyl 4-*O*-benzyl-α-L-rhamnopyranoside by an allylation (at HO-2, to yield **9**), benzylation, and deallylation (with Pd–C, in aqueous ethanol containing acetic acid[25]) sequence In the ^{1}H-n m r spectra of the 2,4-disubstituted benzyl (methyl) α-L-rhamnopyranosides[14], after removal of the *H*-C-3-O*H* coupling by deuteration with D_2O, a characteristic pattern of a doublet of doublets appears at δ ~3 9–4 0 p p m , with $J_{2,3}$ ~3 5 and $J_{3,4}$ ~9 Hz, which does not overlap with other resonances Interestingly, of all 2,4- and 3,4-disubstituted benzyl or methyl α-L-rhamnopyranoside pairs prepared so far, the 2,4-disubstituted derivative has the higher R_F value, on Kieselgel, with a variety of solvents

Using Hg(CN)$_2$ as the catalyst and proton acceptor[5] (Helferich conditions), compounds **10** and **7** gave, in acetonitrile, the protected disaccharide **14** which, on Zemplén deacetylation, yielded **15**, from which the free dirhamnoside **19** was obtained by catalytic hydrogenolysis, as an ~2 1 equilibrium mixture (^{13}C-n m r) of the α and β anomers. Analogously, reaction of **10** and **8**, followed by deacetylation, yielded **21**, from which the (1→2)-linked dirhamnoside **20** was obtained by hydrogenolysis In **20**, the α β anomeric ratio in equilibrium is ~9 1 (^{13}C-n m r) In both

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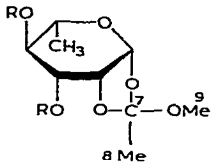
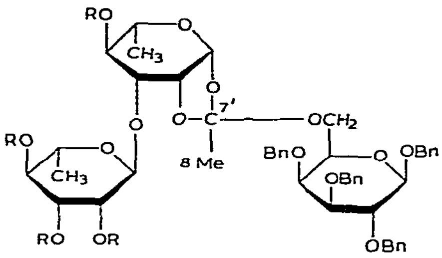
*This ratio is much higher than that obtained with 4,6-*O*-benzylidenehexopyranosides[22] Under conditions identical to those used in the preparation of **7** we found that benzyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**37**) gave an ~3.2 mixture of the 2- and 3-benzyl ether of **37**, whereas benzyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**38**) yields[23] with methyl iodide, under the conditions reported[14], an ~5 4 mixture of the 2-*O*- and 3-*O*-methyl derivative of **38** Our data, and those reported by Garegg *et al*[22,24], reflect the delicate influence of both the substrate and the reagent upon the degree of regioselectivity in this type of reaction



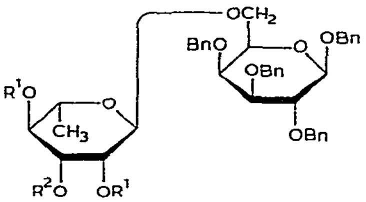
26 R = Ac

27 R = Bn

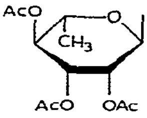


28 R = Ac

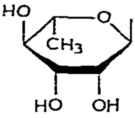
29 R = H



30 R^1 = Ac, R^2 =

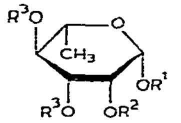


31 R^1 = H R^2 =



32 R^1 = R^2 = Ac

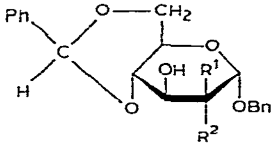
33 R^1 = R^2 = H



34 R^1 = R^2 = R^3 = Ac

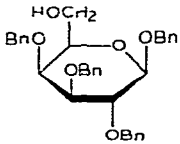
35 R^1 = R^2 = H, R^3 = Ac

36 R^1 = R^2 = H R^3 = Bn



37 R^1 = OH R^2 = H

38 R^1 = H R^2 = OH



39

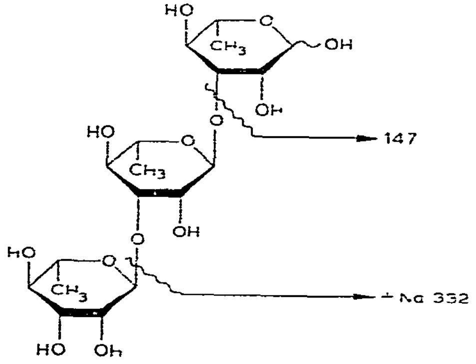
of these α-L-rhamnosylation reactions were detected small amounts of unidentified side-products which must have been formed by hydrolysis of **10** In separate experiments, hydrolysis of **10**, under various conditions, gave readily crystallizable, stable 1,3,4-tri-*O*-acetyl-β-L-rhamnopyranose[26], previously isolated by Laffite *et al*[9] from the reaction mixture obtained after glycosylating with **10**

Catalytic hydrogenolysis of **14**, followed by acetylation, yielded a 3 2 mixture (g l c.) of peracetylated dirhamnosides **16** and **17**, giving rise to resonances for H-1α* at 6 0 p p m and for H-1β at** 5 8 p p m Treatment of this mixture with hydrogen bromide in acetic acid containing some acetic anhydride[28] yielded crystalline 2,4-di-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl bromide[1 9] (**18**) The anomeric configuration of **18** at C-1 was ascertained by the chemical shift of H-1 (δ 6 3 p.p m in the spectrum of **10**, H-1 appears at the same position[5]), and by its high, negative optical rotation

Reaction of **18** with **7** and **8**, under the Helferich conditions, gave the protected trisaccharides **22** and **24** Deprotection of **22** and **24** (Zemplen deacetylation, and then H_2/Pd–C) gave the free trisaccharides **23** and **25**, respectively The ratio of the α and β anomers (at the reducing end) in **23** is ~2 1, and, in **25** ~9 1 (by ^{13}C-n m r , see later)

No appreciable amount of by-products containing benzyl groups was formed in the reaction of **18** with either **7** or **8** However when **18** reacted with benzyl 2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (**39**) under Helferich conditions an ~3 2 mixture of benzyl 2,3,4-tri-*O*-benzyl-6-*O*-[2,4-di-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl]-β-D-galactopyranoside (**30**) and 4-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-L-rhamnopyranose 1 2-(1,2 3,4-tetra-*O*-benzyl-β-D-galactopyranose-6-yl) orthoacetate (**28**) was formed Compounds **28** and **30** co-chromatographed in several solvents, and could only be separated, after deacetylation, as the parent sugars Deprotection of **30** gave *O*-α-L-rhamnopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→6)-D-galactopyranose having physical properties and ^{13}C-n m r spectrum identical to those already described[9 29] This trisaccharide occurs in Nature in both the free[30] and glycosidically linked form[31] The structure of **28** was proved by ^{13}C-n m r. spectroscopy (see later) and by its positive orthoester test[32]

Neither **23** nor **25** gave a molecular ion (M^+) in its field-desorption, mass spectrum The spectra of both **23** and **25** gave an (M + Na) ion at *m/z* 479, an



Scheme 1

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*Numbering begins at the reducing-end unit

**The H-1 signal of α-L-rhamnosides always appears at lower field than that of the corresponding β anomer[9 27]

(M − H + Na) ion at *m/z* 478, and fragment ions at *m/z* 147 and 332, corresponding to the fragmentation depicted in Scheme 1.

The assignments of the ^{13}C-n.m.r. spectra of the compounds described are reported in Table I.

The assignments of the ^{13}C-n.m.r. spectra of the protected disaccharides **14**, **15** and **21** were based on those for the benzylated, reducing-end units (**7** and **8**) and for methyl α-L-rhamnopyranoside (**2**) and methyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranoside (**3**). The introduction of the 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl group into **7** shifted the C-3 signal for **14** downfield by 6.9 p.p.m., relative to that of that carbon atom in **7**. Nearly the same downfield shift (6.6 p.p.m.) was observed for the deacetylated derivative **15**. The C-1′ signals of **14** and **15** are deshielded by 7.3 and 6.4 p.p.m., respectively, relative to those of these carbon atoms in 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranose (**4**) and in **13**. In **21** the α-L-rhamnopyranosyl group on O-2 shifts the C-2 signal downfield by 6.6 p.p.m. In **21**, deshielding of C-1′, relative to that carbon atom in **13**, is 6.3 p.p.m. It is noteworthy that the introduction of either the α-L-rhamnopyranosyl or the 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl group to O-3 of **7** shifts the C-5 signal downfield by ~1 p.p.m., whereas the α-L-rhamnopyranosyl group in **21** shifts those of C-4 and C-5 downfield by 0.4 and 0.6 p.p.m., respectively. The α-L interglycosidic linkage in the dirhamnosides **14**, **15**, and **21** is supported by the position of the C-5′ line, which in each case is under 69 p.p.m. (see refs. 26 and 27).

The resonances of the peracetylated dirhamnoside **16** were assigned with reference to the spectrum of **3**, taking into account that, for α-L-rhamnopyranosides bearing acetyl groups on O-1 and -2, the C-1 signal appears[26] at ~91 p.p.m. and the observation that, if C-1 bears an α-acetoxyl group, the C-5 signal appears[26] at under 71 p.p.m. In **16**, the C-1′ and C-5′ atoms are deshielded by 6.9 and 1.2 p.p.m., respectively, relative to the corresponding carbon atoms in **4**. The C-3 line in **16** is shifted upfield by 3.8 p.p.m. in comparison with the corresponding carbon atom in the free dirhamnoside **19** (see later). This shielding value is in good agreement with the sum of the shielding contributions of the individual acetoxyl groups at C-1α, C-2, and C-4 (0.3, 1.4 and 1.6 p.p.m., respectively), calculated from the ^{13}C-n.m.r. chemical-shift data of partially acetylated L-rhamnose derivatives[26] on the basis of the assumption that the acetyl groups do not interact with each other. Evidence for the α linkage at C-1 in **16** comes from the coupling constant ($^1J_{C-1,H-1}$ 177 Hz), a value that is in agreement with the corresponding coupling-constant of other L-rhamnopyranose derivatives[26] bearing an α-acetoxyl group at C-1, and is ~7–10 Hz larger than the corresponding coupling-constants in various alkyl α-L-rhamnopyranosides[26,27]. In the proton-coupled, ^{13}C-n.m.r. spectrum of **16**, the C-1′ signal appears as a doublet of doublets, with a spacing of 172 Hz ($^1J_{C-1,H-1}$) corresponding to the α interglycosidic linkage, and with a splitting of 4.6 Hz, due to the $^3J_{C-1,H-3}$ inter-residue coupling. In the spectrum of **17**, the resonance lines of the C-3 and C-5 atoms appear at 1.9- and 3.0-p.p.m. lower fields than the corresponding atoms in **16**, in good agreement with the shifts of the corresponding signals (1.9 and 2.6 p.p.m., respectively)

TABLE I

^{13}C-N.M.R. DATA^{a} FOR THE COMPOUNDS REPORTED HEREIN

Atom	*Compound*																		
	$2^{33,b}$	$19\alpha^{c}$	$19\beta^{c}$	$23\alpha^{c}$	$23\beta^{c}$	$20^{2,c}$	7^{b}	8^{b}	14^{b}	15^{b}	21^{b}	16^{b}	17^{b}	22^{b}	24^{b}	25^{c}	30^{b}	28^{b}	$3^{20,b}$
C-1		94.6	94.1	94.6	94.1	93.4	96.5	98.7	96.7	97.0	98.3	90.9^{e}	91.1^{f}	96.4	97.9	93.4	102.9	103.0	
C-2		71.1	71.5	72.0	71.6	79.9	78.9	68.7	78.2	78.0	74.6^{α}	70.4	69.9	78.6	75.3	79.6	82.5	82.3	
C-3		78.5	81.0	78.5	81.8	70.9^{α}	71.8	80.2	78.7	78.4	79.8	74.7	76.6	78.7	79.5	70.8	79.6	79.5	
C-4		72.4	72.6	72.4	72.6	73.2	82.4	80.2	80.9	81.6	80.6	72.2		80.8	80.0	73.4	75.2	75.0	
C-5		69.2	73.0	69.2	73.0	69.1^{β}	67.6	67.8	68.7	68.5	68.4	68.6^{α}	71.6	68.6^{α}	68.3	69.1	73.5	73.3	
C-6		17.5		17.5		17.3	18.1	18.1	18.1	18.1	18.1	17.5		18.1	18.1	17.6	67.3	67.2	
CH_2-1								69.1	69.3^{α}	69.2	69.1			69.2	69.0				
CH_2-2									72.5	73.8^{α}				72.8					
CH_2-3								72.0			72.4				72.6				
CH_2-4								75.2	75.4	75.4	75.3^{α}			75.4	75.9				
C-1′	101.1	102.7		102.5		102.8			99.4	101.6	101.5	99.0^{e}		99.0	98.7	102.4	98.0	97.4	
C-2′	71.0	72.0		70.8^{α}		70.5^{α}			70.1	71.2^{α}	71.7^{β}	70.2		71.5	72.3^{α}	70.0	70.9	78.4^{α}	
C-3′	71.8	71.0		79.0		70.9^{α}			69.2^{α}	71.9^{α}	71.1^{β}	69.1^{α}		74.9	74.4	78.4	75.2	78.7^{α}	
C-4′	73.0	73.0		72.2		72.8			71.3	72.8^{α}	73.0	70.9		72.4	71.2^{α}	72.2	73.5	71.1^{β}	
C-5′	68.2	69.7		69.7^{β}		69.8^{β}			67.0	68.7	68.9	67.5		67.4	67.3	69.7	67.2	69.5	
C-6′	17.5	17.7		17.5		17.6			17.5	17.5	17.6	17.4		17.5^{β}	17.3	17.6	17.4	17.7	
C-7′																		124.5	
C-8′																		24.7	
C-9′																			
C-1″				102.8										99.4	99.2	102.7	98.9	99.6	99.0
C-2″				71.0^{α}										68.7^{α}	70.4	71.0	70.3	70.1	70.3
C-3″				71.1^{α}										70.6	68.7	71.2	68.7	69.0	70.0
C-4″				73.0										71.1	71.0	73.0	70.9	70.8^{β}	70.7
C-5″				69.9^{β}										67.3	67.3	69.7	66.9	67.2	68.5
C-6″				16.7										17.4^{β}	17.3	16.9	17.4	17.4	17.3

Atom	*Compound*													
	26^{b}	**27**^{b}	**39**^{b}	**32**^{31,b}	**33**^{31,b}	**4**^{27,b}	**35**^{b}	**36**^{b}	**11**$\alpha^{c,d}$	**11**$\beta^{c,e,f}$	**12**$\alpha^{c,g}$	**12**$\beta^{c,h}$	**13**α^{c}	**13**β^{c}
C-1			103.2^{i}	103.0	103.0		93.9	94.1	91.6^{l}	94.7	94.75	94.4		
C-2			82.5	82.5	82.5		70.0	69.2	81.7^{m}	82.4	67.8	68.1		
C-3			79.7	79.7	79.6		73.7	81.7	70.8^{n,o}	74.1	80.5	82.9		
C-4			75.1$^{\alpha}$	75.2	75.2		71.8$^{\alpha}$	79.7	73.5^{p}	73.1	72.0	71.6		
C-5			75.0$^{\alpha}$	73.6	73.8		70.3$^{\alpha}$	71.5	68.9^{q}	72.8	69.1	72.7		
C-6			61.9	67.2	67.6		17.5	18.0						
CH_2-1														
CH_2-2														
CH_2-3		72.1												
CH_2-4		75.3												
C-1′	97.4	97.5		98.3	100.9	92.1							94.7	94.2
C-2′	77.1	77.2		69.3	71.1	70.9							71.7	72.1
C-3′	71.0$^{\alpha}$	79.5$^{\alpha}$		70.0	71.5	69.3							70.9	73.6
C-4′	70.7$^{\alpha}$	79.3$^{\alpha}$		71.3	72.7	71.6							73.1	72.7
C-5′	69.3	70.4		66.7	68.6	66.3							68.9	72.7
C-6′	17.6	18.1		17.4	17.6	17.5							17.6	17.6
C-7′	124.5	123.8												
C-8′	24.6	24.4												
C-9′	49.7	49.6												
C-1″														
C-2″														
C-3″														
C-4″														
C-5″														
C-6″														

[a] The assignments marked with an identical Greek letter may be reversed in each vertical column. [b] Recorded in $CDCl_3$. [c] Recorded in D_2O. [d] OCH_3 59.4 p.p.m. [e] $^{1}J_{C-1,H-1}$ 159.3 Hz. [f] OCH_3 62.6 p.p.m. [g] $^{1}J_{C-1,H-1}$ 169.5 Hz. [h] $^{1}J_{C-1,H-1}$ 157.3 Hz. [i] $^{1}J_{C-1,H-1}$ 177 Hz. [j] $^{1}J_{C-1,H-1}$ 165 Hz. [k] $^{1}J_{C-1,H-1}$ 159 Hz. [l] $^{1}J_{C-1,H-1}$ 169.3 Hz. [m] $^{1}J_{C-2,H-2}$ 146 Hz. [n] $^{1}J_{C-3,H-3}$ 148 Hz. [o] $^{1}J_{C-3,H}$ 6.5 Hz. [p] $^{1}J_{C-4,H-4}$ 150 Hz. [q] $^{1}J_{C-5,H-5}$ 145.5 Hz. [r] $^{1}J_{C-1,H-1}$ 172 Hz, $^{3}J_{C-1,H-1}$ 4.6 Hz.

in the spectrum of 1,2,3,4-tetra-*O*-acetyl-β-L-rhamnopyranose[26] (**34**) relative to those in that of the α anomer (**5**).

The assignment of resonance lines in the ^{13}C-n.m.r. spectra of **22** and **24** was made with reference to the spectra of **8**, **14**, and **21**, taking into account the α-L-rhamnosylation shifts. The nature of the interglycosidic linkages in **22** and **24** is reflected in the position of the lines of the C-5′ and C-5″ atoms (under 68 p.p.m.). The assignment of the ^{13}C-n.m.r. lines of **30** proved possible by considering the spectra of **22**, benzyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**32**), and **39**. In **30** the α-L interglycosidic linkages are supported by the positions of the C-5′ and C-5″ lines (67.2 and 66.9 p.p.m., respectively).

Spectral assignment for **28** was aided by that for 3,4-di-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-β-L-rhamnopyranose[26] (**26**), in which the lines corresponding to C-1, -6, -8, and -9 were recognized by using the known chemical-shifts[35] of these atoms. The line at 124.5 p.p.m. is assigned to C-7, considering the chemical-shift range[36] of the carbon atom in the HC(O-)$_3$ structure. In the spectrum of **26**, the assignment of the line at 77.1 p.p.m. to C-2 was corroborated by the observation that replacement of the acetyl groups by benzyl groups, to give 3,4-di-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-β-L-rhamnopyranose[26] (**27**) left this resonance virtually unaffected. In the spectrum of **28** the resonances of the ring-carbon atoms of the reducing-end unit almost coincide with those observed for the corresponding carbon atoms in **30**, and this is also true for those of the nonreducing-end unit, as compared with the corresponding carbon atoms in **30** except for an 0.7-p.p.m. downfield-shift for C-1″. The carbon resonance lines of the middle sugar unit were assigned with reference to those in the spectra of **26** and **27**.

The orthoester structure results in characteristic resonances at 24.5 ±0.2 p.p.m. for the methyl carbon atom (C-8) and at 124 ±0.5 p.p.m. for the C-7 atom, linked to three oxygen atoms. As neither of these resonances is in the vicinity of other resonances commonly found in the ^{13}C-n.m.r. spectra of free or protected carbohydrates they can be used for the identification of this structural unit.

A comparison of the ^{13}C-n.m.r. spectrum of 3,4-di-*O*-acetyl-β-L-rhamnopyranose[26] (**35**) with that of **26**, and of 3,4-di-*O*-benzyl-β-L-rhamnopyranose (**36**) with that of **27**, shows that the formation of the orthoester structure at the equatorial HO-1 and the axial HO-2 groups induces a downfield shift of 3.5 for the C-1, and 7–8 p.p.m. for the C-2 atom.

The line of C-5 in the ^{13}C-n.m.r. spectra of **26** and **27**, and the line of C-5′ in that of **28** appear at ~70 p.p.m., which is ~3 p.p.m. less than the average value for the C-5 atom in the spectra of various β-L-rhamnopyranosides[27]. We ascribe this difference (and also that found between the chemical shift for the C-5 atoms of **26** and **27**, relative to those for the corresponding carbon atoms in **35** and **36**, respectively) to changes in the dihedral angles of the L-rhamnopyranose ring by the attachment of the dioxolane skeleton to C-1 and C-2 relative to the $^4C_1$(L) conformation; this is supported by the ^{1}H-n.m.r. data[16].

The signal for C-6 (methyl) carbon atoms in the protected L-rhamnopyranosides appears at 18.1 p.p.m. if HO-4 bears a benzyl substituent, and at ~17.6 p.p.m. if HO-4 is either free or acetylated.

In the ^{13}C-n.m.r. spectra of benzyl-protected L-rhamnose derivatives, the resonance line of the methylene carbon atom in the benzyl group attached to O-1 is invariably found at ~69 p.p.m., whereas that of that attached to O-4 lies between 75.2 and 75.9 p.p.m. The recognition of these resonances may make the assignment of the sugar carbon atoms easier. In this context, it should be noted that the methylene carbon atom of benzyl alcohol is deshielded by ~4.6 p.p.m. by α-L-rhamnopyranosylation (cf. ref. 27), and by ~6.6–6.8 p.p.m. by β-D-galacto- and β-D-gluco-pyranosylation[37], the resonance line of the methylene carbon atom in the spectrum of benzyl alcohol being[38] at 64.5 p.p.m.

The spectrum of **20** was explained with reference to that of the anomers of 2-*O*-methyl-L-rhamnopyranose[39] (**11**), in which the line for C-1α appears at 91.6 p.p.m., and that for C-1β, at 94.7 p.p.m., the intensity ratio being ~3:1. These assignments are verified by the values of $^1J_{C-1,H-1}$ (see Table I). These lines are respectively shifted 3.1 p.p.m. upfield and 0.5 p.p.m. downfield, relative to the displacement of the C-1 signals in the ^{13}C-n.m.r. spectrum of α- and β-L-rhamnopyranose. The finding that, in the spectrum of a rhamnose derivative, the C-1α atom resonates at a higher field than the corresponding C-1β atom is unusual, taking into account that the C-1 atoms in α-L-rhamnopyranose in various α-L-rhamnopyranosides[27] and in 2-*O*-β-D-gluco- and -galacto-pyranosyl-α-L-rhamnopyranoses[40] resonate at a lower field than those of the corresponding β anomers, and it shows that the shift contributions of the individual substituents may vary considerably as a function of the anomeric configuration. A peculiarity of the spectrum of **11α** is the relatively large coupling-constant between C-3 and H-6 ($^4J_{C-3,H-6}$ 5 Hz), verified by $^{13}C\{^1H\}$, selective heteronuclear-decoupling.

In the spectrum[2] of **20**, the C-1α resonance appears at 93.4 p.p.m., and the C-1β, at 93.9 p.p.m. The intensity ratio of these lines is ~9:1. These lines are respectively 1.4 and 0.3 p.p.m. upfield, relative to the C-1 line of α- and β-L-rhamnose. They are assigned with reference to the spectrum of **11** and to the published[10] ^{1}H-n.m.r. data for H-1 in **20**, taking into account that, for L-rhamnose, H-1α resonates[41] at a lower field than H-1β. As the position of the C-5 resonance is highly sensitive to the anomeric configuration of L-rhamnose[40] and of its derivatives[26,27], the assignment of the line at 69.1 p.p.m. to C-5, the intensity of which is comparable to that of the line at 93.4 p.p.m., further corroborates our assignment of the resonance line at 93.9 p.p.m. to C-1β.

An assignment of the ^{13}C-n.m.r. spectrum of **19** had been given by Laffite *et al.*[29]. Our approach to the assignment of the ^{13}C-n.m.r. spectral lines of **19** was aided by a study of the spectrum of 3-*O*-methyl-L-rhamnose[39] (**12**), in which the line of C-1α has the same chemical shift as the corresponding carbon atom of L-rhamnose, while C-1 is deshielded by 0.2 p.p.m. For **12**, the C-3 line is respectively shifted downfield by 9.6 p.p.m. for the α, and by 9.3 p.p.m. for the β anomer. For **12α**, the C-2

TABLE II

COMPARISON OF THE ^{13}C-N.M.R. CHEMICAL-SHIFTS INDUCED IN α- AND β-L-RHAMNOPYRANOSES BY METHYL AND α-L-RHAMNOPYRANOSYL GROUPS

Derivative of α-L-rhamnopyranose	$\Delta\delta^a$ (*p.p.m.*) *C-1*	*C-2*	*C-3*	*C-4*	*C-5*
2-*O*-methyl	−3.1	−10.0	−0.1	−0.1	0
2-*O*-α-L-rhamnopyranosyl	−1.3	−8.2	0.0	−0.1	−0.2
3-*O*-methyl	0.0	−3.9	+9.6	−1.1	−0.2
3-*O*-α-L-rhamnopyranosyl	−0.1	−0.6	+7.6	−0.7	+0.3
Derivative of β-L-rhamnopyranose					
2-*O*-methyl	−0.5	−10.3	−0.5	−0.3	−0.1
2-*O*-α-L-rhamnopyranosyl	−0.3	+7.8	—	—	—
3-*O*-methyl	−0.2	−4.0	−9.3	−1.1	0
3-*O*-α-L-rhamnopyranosyl	−0.1	−0.6	−7.4	−0.1	+0.3

[a] $\Delta\delta$ refers to the difference (in p.p.m.) between the chemical shifts of the corresponding carbon atoms in L-rhamnopyranose and the derivatives. Positive sign indicates deshielding.

and C-4 signals are shifted upfield by 3.9 and 1.1 p.p.m., respectively*. The introduction of the α-L-rhamnopyranosyl group onto HO-3 of L-rhamnose induces a downfield shift of 7.6 p.p.m. for the C-3α and 7.4 p.p.m. for the C-3β atoms. For **19α**, the C-2 atom is deshielded by 0.3 p.p.m., relative to C-2 of α-L-rhamnopyranose which is in contrast with the upfield shift of C-2 induced by a methyl group at O-3, and is in agreement with the earlier finding of Colson and King[40], who "did not observe a significant change in the chemical shift of C-2(α) of the L-rhamnose residue on disaccharide formation at position 3". On the other hand, for **12α**, C-4 is shielded by 1.1 p.p.m., which agrees well with the shielding of C-4 in **19α** (0.7 p.p.m.) relative to C-4 of α-L-rhamnopyranose. For **19α**, C-1′ appears at 8 p.p.m. lower field than for C-1 of α-L-rhamnopyranose, while the signal for C-2′ is shifted 0.6 p.p.m. upfield, relative to the corresponding atom in α-L-rhamnopyranose.

The ^{13}C-n.m.r. chemical-shifts induced in α-L-rhamnopyranose by methyl and α-L-rhamnopyranosyl groups are summarized in Table II. The methylation shift at the α carbon atom (*i.e.*, at that to which O-Me is linked) represents well the shift induced by α-L-rhamnopyranosylation. On the other hand, for the β carbon atoms, the shifts that are induced by a methyl group may differ considerably from those induced by an α-L-rhamnopyranosyl group.

The spectrum of **25** was assigned with reference to the spectra of **19α** and **20**.

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*Both the sense and the magnitude of the methylation shifts in L-rhamnose methyl ethers agree well with those found by Gorin[12] for methyl ethers of D-mannose.

The C-1β line in this case also appears at a lower field (by 0.5 p.p.m.) than the C-1α, and the C-1′β is at a higher field than the C-1′α line.

The spectrum of **23α** and **23β** may be explained by using that of **19α** and **19β**, taking into account the α-L-rhamnosylation shifts, as already discussed. It is noteworthy that the middle L-rhamnosyl residue gives rise to broader resonance lines with reference to the lines of the (nonreducing) L-rhamnosyl group, as a consequence of its slower relaxation.

This ^{13}C-n.m.r.-spectral study of free and protected di- and tri-rhamnosides and mono- and di-rhamnosyl-D-galactopyranosides led to the following conclusions. (*a*) Upon introduction into the benzyl-protected α-L-rhamnopyranosides **7** and **8**, the downfield chemical-shift induced by the α-L-rhamnopyranosyl group at the α-carbon atom is in the range of 6.6–6.9 p.p.m., which is not appreciably influenced by the substituents on the glycosylating L-rhamnosyl group [see also, the ^{13}C-n.m.r. chemical-shifts of benzyl 3,4-di-*O*-benzyl-2-*O*-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside[2]]. For the free di- and tri-rhamnosides (**19**, **20**, **23**, and **25**) the magnitude of the downfield shift on α-L-rhamnosylation at the α-carbon atom is ~1 p.p.m. higher, and falls in the range of 7.4–8.2 p.p.m. On the other hand, α-L-rhamnosylation at O-6 of D-galactopyranose induces an ~5.7-p.p.m. downfield shift for C-6, irrespective of whether the other hydroxyl groups of the D-galactose residue are free[29] or protected. (*b*) In all free di- and tri-rhamnosides herein described, the signals of the C-5α atoms appear at 69.1–69.2 p.p.m., only slightly displaced from the corresponding line of α-L-rhamnopyranose (68.9 p.p.m.), whereas the lines both for C-5′ and C-5″ are in the range of 69.7–69.9 p.p.m. (*c*) In each di- and trisaccharide reported herein, the C-1 signal of the nonreducing rhamnosyl residues are deshielded by 7–8 p.p.m. when the "aglycon" is an L-rhamnopyranose residue linked through either HO-2 or HO-3, and by ~6 p.p.m. when the "aglycon" component is a β-D-galactopyranose residue linked through HO-6.

EXPERIMENTAL

General. — Melting points were measured on a Kofler hot-stage and are uncorrected. All compounds were dried at ~30°/15–20 Pa. Thin-layer chromatography was performed on precoated layers of silica gel (Merck) with detection by charring with 50% aqueous sulfuric acid, or by ultraviolet light in the case of the benzylated derivatives. ^{13}C-N.m.r. spectra were recorded with a Varian XL-100-FT spectrometer at 25.16 MHz for solutions in chloroform-*d*, and, for compounds **11**, **12**, **13**, **19**, **20**, **23**, and **25**, in D_2O, using 8k data points, with proton-noise decoupling. Coupling constants were determined by the gated, decoupling technique. Chemical shifts are given relative to internal 1,4-dioxane (67.3 p.p.m.) for D_2O solutions, and to internal Me_4Si for chloroform-*d* solutions. Optical rotations were measured with a Perkin–Elmer 241 automatic polarimeter. Field-desorption, mass spectra were recorded with a Vg Micromass 2AB 2F instrument equipped with a Vg 2035 data system.

Benzyl 3,4-di-O-benzyl-α-L-rhamnopyranoside (**8**) — Benzyl 2-*O*-allyl-4-*O*-benzyl-α-L-rhamnopyranoside[14] (1 75 g) was stirred with benzyl chloride (10 mL) and powdered potassium hydroxide (5 g) for 3 h at 100° The mixture was then diluted with chloroform filtered and the filtrate steam-distilled The residual, yellowish oil, isolated in the usual way, was dissolved in ethyl alcohol (10 mL), the solution added to acetic acid (10 mL), water (10 mL), and 10% Pd–C (500 mg), and the mixture stirred for 6 h at 90° The usual processing, followed by chromatographic purification on Kieselgel H (150 g), with 3 2 ethyl acetate–light petroleum as the eluant gave **8** (1 30 g, 51%), $[\alpha]_D$ −49° (*c* 1 0, chloroform), lit [14] $[\alpha]_D$ −49°

Benzyl 2 4-di-O-benzyl-3-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**14**) – A mixture of compound **7** (ref 14 3 0 g), $Hg(CN)_2$ (2 g), powdered 4 A molecular sieve (3 g), and **10** (4 3 g) in MeCN (20 mL) was stirred for 2 h at room temperature The usual processing followed by chromatography on Kieselgel H (200 g) with 4 1 ethyl acetate–light petroleum, gave **14** (4 6 g, 94%) as a colorless syrup, $[\alpha]_D$ −57° (*c* 1, chloroform)

Anal Calc for $C_{39}H_{46}O_{12}$ C, 66 29, H, 6 51 Found C, 66 45, H, 6 40

Benzyl 3,4-di-O-benzyl-2-O-α-L-rhamnopyranosyl-α-L-rhamnopyranoside (**21**) — A mixture of **10** (2 g), **8** (1 g), $Hg(CN)_2$ (1 g), powdered 4 A molecular sieve (3 g), and MeCN (5 mL) was stirred for 24 h at room temperature Compound **10** (3 g) was then added, and stirring was continued for 24 h The usual processing gave a syrup which was dissolved in methanol (30 mL) containing a catalytic amount of NaOMe After being kept overnight, the solution was made neutral with acetic acid, evaporated to dryness, and the residue dissolved in chloroform (40 mL) The solution was washed with water (3 × 20 mL) dried (Na_2SO_4), and evaporated The residual syrup was purified by chromatography on Kieselgel H (100 g), using 3 1 benzene–methanol, to give syrupy **21** (1 3 g), $[\alpha]_D$ −55 6° (*c* 0 6, chloroform)

Anal Calc for $C_{33}H_{40}O_9$ C, 68 27, H, 6 89 Found C, 68 0 H, 6 80

Benzyl 2,4-di-O-benzyl-3-O-α-L-rhamnopyranosyl-α-L-rhamnopyranoside (**15**) — A solution of **14** (600 mg) in methanol (20 mL) was treated with a catalytic amount of NaOMe for 3 h and then with Amberlite IR-120 (H^+) and IR-4B (HO^-) resins followed by evaporation, to yield syrupy **15** (440 mg, 89%), $[\alpha]_D$ −59° (*c* 1 3, chloroform)

Anal Calc for $C_{33}H_{40}O_9$ C, 68 27 H, 6 89 Found C, 68 10, H, 6 95

3-O-α-L-Rhamnopyranosyl-L-rhamnopyranose[1] (**19**) — To a solution of **15** (400 mg) in a mixture of 96% ethanol (20 mL) and acetic acid (1 mL) was added 10% Pd–C (200 mg), and the mixture was hydrogenated under atmospheric pressure and room temperature for one day The usual processing gave **19** (200 mg) as a glassy residue, $[\alpha]_D$ −31 2° (*c* 0 7, water), lit [9] $[\alpha]_D$ −21° (*c* 3 2, water)

Anal Calc for $C_{12}H_{22}O_9$ C, 46 45, H, 7 09 Found C, 46 28, H, 7 16

2-O-α-L-Rhamnopyranosyl-L-rhamnopyranose[2] (**20**) — Compound **20** was prepared from **21**, as described for **19** Amorphous **20** had $[\alpha]_D$ −24° (*c* 0 8, water) lit [10] $[\alpha]_D$ −28 7° (water)

Anal Calc for $C_{12}H_{22}O_9$ C, 46 45, H, 7 09 Found C 46 90, H 7 25

1,2,4-Tri-O-acetyl-3-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-α,β-L-rhamnopyranose (**16**, **17**). — Compound **14** (4.0 g) in 96% ethanol (100 mL) was hydrogenated overnight in the presence of 10% Pd–C (1 g). The usual processing followed by chromatography on Kieselgel H (150 g) using 3:1 benzene–methanol as the eluant, gave 3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-L-rhamnopyranose (2.35 g, 95%), $[\alpha]_D$ −48.3° (*c* 0.6, acetone), as a syrup. This syrup was acetylated with 1:1 acetic anhydride–pyridine (20 mL); the usual processing gave a syrupy 3:2 mixture of **16** and **17**.

Anal. Calc. for $C_{24}H_{34}O_{15}$: C, 51.24; H, 6.04. Found: C, 51.30; H, 6.12.

2,4-Di-O-acetyl-3-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl bromide[1] (**18**). — A 3:2 mixture of **16** and **17** (1700 mg) was dissolved in a mixture of acetic acid (15 mL) and acetic anhydride (1.5 mL). The solution was chilled, treated with 33% hydrogen bromide in acetic acid (10 mL, Fluka), kept for 1 h at 5° and for 30 min at room temperature, diluted with chloroform (200 mL), washed with water (10 × 50 mL), dried (Na_2SO_4), and evaporated to dryness below 25°. The residual foam was dissolved in ether (20 mL), and hexane (100 mL) was added; **18** separated as a colorless, crystalline mass (1360 mg, 77%), m.p. 106–109°, $[\alpha]_D$ −97.8° (*c* 1.9, chloroform).

Benzyl 2,4-di-O-benzyl-3-O-[2,4-di-O-acetyl-3-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl]-α-L-rhamnopyranoside (**22**). — A solution of **18** (2 g) in MeCN (20 mL) was added dropwise to a stirred mixture of **7** (2.6 g), $Hg(CN)_2$ (1.7 g), powdered 4 A molecular sieve (3 g), and MeCN (10 mL) during 30 min, and stirring was continued overnight. The usual processing, followed by chromatography on Kieselgel H (350 g) using 100:3 benzene–methanol, gave **7** (1.1 g), and **22** (1370 mg, 42.6% based on **18**), as a syrup, $[\alpha]_D$ −37° (*c* 0.8, chloroform).

Anal. Calc. for $C_{49}H_{60}O_{18}$: C, 62.82; H, 6.41. Found: C, 62.70; H, 6.50.

Benzyl 3,4-di-O-benzyl-2-O-[2,4-di-O-acetyl-3-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl]-α-L-rhamnopyranoside (**24**). — By reaction of **8** with **18** (as described for **22**), compound **24** was obtained as a syrup in 37% yield, based on **18**. The crude product was acetylated, to facilitate chromatographic separation of **24** from **8** on Kieselgel H using 3:2 light petroleum–ethyl acetate, $[\alpha]_D$ −42° (*c* 0.9, chloroform).

Anal. Calc. for $C_{49}H_{60}O_{18}$: C, 62.82; H, 6.41. Found: C, 62.90; H, 6.40.

O-α-L-Rhamnopyranosyl-(1→3)-O-α-L-rhamnopyranosyl-(1→3)-L-rhamnopyranose[1] (**23**). — Compound **22** (825 mg) was deacetylated as described for **15**, to give syrupy benzyl 2,4-di-*O*-benzyl-3-*O*-(3-*O*-α-L-rhamnopyranosyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside {620 mg, 96.8%, $[\alpha]_D$ −73.5° (*c* 0.7, methanol)}, which was hydrogenolyzed in EtOH (30 mL) and acetic acid (2 mL) in the presence of 10% Pd–C (250 mg, Fluka) for 24 h. The usual processing gave amorphous **23** (320 mg, 82%), $[\alpha]_D$ −48° (*c* 0.4, water).

Anal. Calc. for $C_{18}H_{32}O_{13}$: C, 47.36; H, 7.01. Found: C, 47.50; H, 7.10.

O-α-L-Rhamnopyranosyl-(1→3)-O-α-L-rhamnopyranosyl-(1→2)-L-rhamnopyra-

nose (**25**) — By deacetylation as for **14**, compound **24** yielded benzyl 3,4-di-*O*-benzyl-2-*O*-(3-*O*-α-L-rhamnopyranosyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside as a solid foam (97% yield), $[\alpha]_D$ −66° (*c* 1 0, methanol), which, upon hydrogenolysis, gave amorphous **25** in 86% yield $[\alpha]_D$ −52° (*c* 0 5, water)

Anal. Calc for $C_{18}H_{32}O_{13}$ C, 47 36, H, 7 01 Found C, 47 45, H 7 11

Benzyl 2,3,4-tri-O-benzyl-6-O-[2,4-di-O-acetyl-3-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl]-β-D-galactopyranoside (**30**) *and 4-O-acetyl-3-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-β-L-rhamnopyranose 1,2-(1,2,3,4-tetra-O-benzyl-β-D-galactopyranose-6-yl orthoacetate)* (**28**) — A solution of **18** (1 2 g) in MeCN (8 mL) was added dropwise to a stirred mixture of benzyl 2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (1 11 g), Hg(CN)$_2$ (1 1 g), powdered 4 A molecular sieve (3 g), and MeCN (10 mL) and the mixture was then stirred overnight, and processed as usual Chromatography on Kieselgel H (250 g), with 200 6 1 benzene–methanol–triethylamine as the eluant, gave a co-chromatographing mixture of **28** and **30** as a white, solid foam (1235 mg), this was deacetylated (Zemplén), and the product was chromatographed on Kieselgel H (100 g), with 200 60 1 benzene–methanol–triethylamine, to give 3-*O*-α-L-rhamnopyranosyl-β-L-rhamnopyranose 1,2-(1,2,3,4-tetra-*O*-benzyl-β-D-galactopyranose-6-yl orthoacetate) (**29**) as a syrup, $[\alpha]_D$ −16 5° (*c* 1 2, chloroform), and benzyl 2,3,4-tri-*O*-benzyl-6-*O*-(3-*O*-α-L-rhamnopyranosyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**31**), m p 173–176°, $[\alpha]_D$ −17 8° (*c* 0 6, pyridine) Acetylation of **31** and **29** with 1 1 acetic anhydride–pyridine gave **30** as a syrup, $[\alpha]_D$ −42 3° (*c* 0 3, chloroform), and **28** as a syrup, $[\alpha]_D$ −15 0° (*c* 0 5, chloroform) Compounds **28** and **29** decomposed within a few minutes in a methanolic solution of hydrochloric acid (0 01%) Catalytic hydrogenolysis of **31** in ethanol gave *O*-α-L-rhamnopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→6)-D-galactopyranose, $[\alpha]_D$ −35 5° (*c* 0 25, water); lit [9] $[\alpha]_D$ −40 6° (*c* 0 4, water)

NOTE ADDED IN PROOF

Compound **19** was obtained in crystalline form by D Schwarzenbach and R W Jeanloz, *Carbohydr Res* 81 (1980) 323–329

ACKNOWLEDGMENTS

This work was supported by a Fellowship (to V P) from the Hungarian Academy of Sciences, for studies at the Institute of Biochemistry, L Kossuth University, Debrecen V P expresses his sincerest thanks to Dr R C Pandey of the Frederick Cancer Research Center (Frederick, MD) for recording the mass spectra

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