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SYNTHESIS AND ^{13}C-NMR SPECTROSCOPIC INVESTIGATIONS OF RHAMNOBIOSES

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Abstract—A convenient method has been developed for the synthesis of all mono- and di-O-benzyl ethers of methyl α-L-rhamnopyranoside applying a new stereoselective method for the hydrogenolytic ring-cleavage of benzylidene acetals. Using the prepared dibenzyl ethers as aglycones, the (1→2)-, (1→3)- and (1→4)-linked rhamnosyl-rhamnose derivatives (**13–15**) were synthesised. Hydrogenolysis of the latter compounds and subsequent acetylation gave the pentaacetates (**16–18**) of methyl dirhamnosides, which on saponification furnished the free methyl dirhamnosides (**19–21**). Acetolysis of **16–18** gave the corresponding dirhamnose-hexaacetates which were transformed into the three disaccharides by saponification. The structure of each product was investigated by ^{13}C-NMR spectroscopy, and for the purpose of ^{13}C-NMR studies the mono-O-methyl ethers of methyl α-L-rhamnopyranoside, the diacetates and di-O-benzyl ethers of the latter compounds, and, also the diacetates of methyl α-L-rhamnopyranoside were synthesised.

It has been established that, for ^{13}C-NMR investigations of oligosaccharides, the benzyl ethers of monosaccharides are more suitable model compounds than the currently used monosaccharide methyl ethers.

RHAMNOBIOSIDES are natural products frequently occuring as constituents of several glycolipids,[1-3] plant glycosides[4-6] and bacterial cell-wall polysaccharides.[7-9] Recognising the immunological and immunochemical importance of these immuno-determinant oligosaccharides, great efforts have been made recently towards their synthesis.[10-13] Of the published syntheses, the one dealing with the preparation of O-α-L-rhamnopyranosyl-(1→4)-L-rhamnose[10,11] has to be considered as a definitive synthesis, whereas the methods described for the production of (1→2)[13] and (1→3)[14] linked dirhamnoses are based on the so-called "open-chain" method, introduced by King *et al.*[16-17] which results in the formation of structural isomeric compounds.

We now report on the synthesis of the three possible rhamnopyranosyl-rhamnopyranoses using the di-O-benzyl ethers of methyl α-L-rhamnopyranoside as the aglycones.

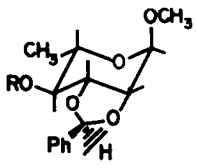
RESULTS AND DISCUSSION

Methyl 3,4-di-O-benzyl-α-L-rhamnopyranoside (**7**) and methyl 2,4-di-O-benzyl-α-L-rhamnopyranoside (**8**) were prepared by the stereoselective hydrogenolysis of methyl 4-O-benzyl-*exo*- (**5**) and methyl 4-O-benzyl-*endo*-2,3 O-benzylidene-α-L-rhamnopyranoside (**6**), respectively. Benzylidenation of methyl α-L-rhamnopyranoside has been performed by several research groups[18-20] but the resulting two isomers could not be separated. Therefore in the present study, the mixture of *endo*- and *exo* isomers, obtained by the benzylidenation of methyl α-L-rhamnopyranoside, was acetylated and the two 4-O-acetyl derivatives (**1** and **2**) were separated by fractional crystallisation. The structure of **1** and **2** was confirmed by both ^{1}H-NMR and ^{13}C-NMR spectroscopic investigations.[21] Saponification of **1** and **2** gave crystalline methyl *exo*-2,3-O-benzylidene- (**3**) and syrupy methyl *endo*-2,3-O-benzylidene-α-L-rhamnopyranoside (**4**), respectively. According to the literature both the *exo* and *endo* isomers of *p*-nitrophenyl[22]- and benzyl 2,3-O-benzylidene-L-rhamnopyranosides[23] have been isolated.

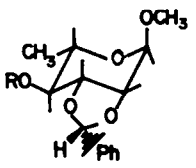
Benzylation of **3** and **4** gave crystalline 4-O-benzyl-*exo* (**5**)[18] and syrupy 4-O-benzyl-*endo* (**6**)[18] derivative, respectively. According to glc examination, the hydrogenolysis[24] of **5**, with a reaction time of 5 min, gave 98.5% of methyl 3,4-di-O-benzyl-α-L-rhamnopyranoside (**7**), contaminated with 1.5% of the corresponding 2,4-di-O-benzyl analogue (**8**). The hydrogenolysis of **6** under similar conditions resulted in a similar proportion of the products, but with the difference of the preferred formation of **8** (96%), accompanied by traces of **7**. For analytical purposes compounds **7** and **8** were purified by column chromatography.

The third aglycone, methyl 2,3-di-O-benzyl-α-L-rhamnopyranoside (**12**) was synthesised as follows. Allylation of methyl 2,3-O-isopropylidene-α-L-rhamnopyranoside, using the method of Brimacombe,[25] gave the syrupy 4-O-allyl derivative (**9**), which on hydrolysis with acetic acid, afforded methyl 4-O-allyl-α-L-rhamnopyranoside (**10**). Benzylation of **10** was carried out using the method of Zemplén[26] to yield the 2,3-O-benzyl derivative (**11**). Removal of the allyl group of **11** was performed using the method of Ogawa,[27] and **12** was obtained in good yield.

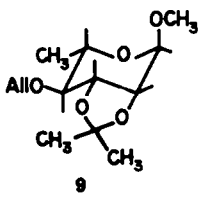
Reaction of **7**, **8** and **12** with α-acetobromo-L-rhamnose gave 95% of crystalline **13**, 78.8% of syrupy **14**, and 67.2% of syrupy **15**, respectively. The structure of the three disaccharide derivatives was proved by ^{13}C-NMR spectroscopy. The chemical shifts of C-1′ and the C-1′-



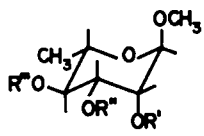
1 R = Ac
3 R = H
5 R = Bzl



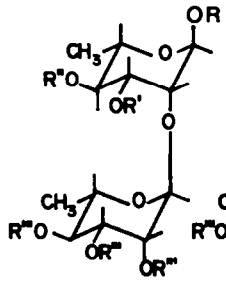
2
4
6



9



7 R′ = H; R″ = R‴ = Bzl
8 R′ = R‴ = Bzl; R″ = H
10 R′ = R″ = H; R‴ = All
11 R′ = R″ = Bzl; R‴ = All
12 R′ = R″ = Bzl; R‴ = H
28 R′ = Bzl; R″ = R‴ = H
29 R′ = R‴ = H; R″ = Bzl
30 R′ = R″ = H; R‴ = Bzl
31 R′ = Bzl; R″ = R‴ = Ac
32 R′ = R‴ = Ac; R″ = Bzl
33 R′ = R″ = Ac; R‴ = Bzl
34 R′ = H; R″ = R‴ = Ac
35 R′ = R‴ = Ac; R″ = H
36 R′ = R″ = Ac; R‴ = H
37 R′ = R″ = R‴ = Bzl
38 R′ = CH₃; R″ = R‴ = Bzl
39 R′ = R‴ = Bzl; R″ = CH₃
40 R′ = R″ = Bzl; R‴ = CH₃
41 R′ = CH₃; R″ = R‴ = Ac
42 R′ = R‴ = Ac; R″ = CH₃
43 R′ = R″ = Ac; R‴ = CH₃
44 R′ = CH₃; R″ = R‴ = H
45 R′ = R‴ = H; R″ = CH₃
46 R′ = R″ = H; R‴ = CH₃



R = CH₃; R′ = R″ = Bzl; R‴ = Ac
13 14 15
R = CH₃; R′ = R″ = R‴ = Ac
16 17 18
R = CH₃; R′ = R″ = R‴ = H
19 20 18
R = R′ = R″ = R‴ = Ac
22 23 24
R = R′ = R″ = R‴ = H
25 26 27

H-1′ coupling constant (**13**: 99,3 ppm, **14**: 99.4 ppm, $^1J_{CH}$ = 174 Hz, and **15**: 99.3 ppm) unequivocally prove the α-L-(1*C*) configuration of the interglycosidic bonds.

Catalytic hydrogenation of **13–15** followed by acetylation, gave the corresponding crystalline methyl dirhamnoside peracetates (**16–18**) respectively. Compound **17** has been recently prepared, but the m.p. of our sample is 10° higher than the value given by Laffite *et al.*[14] The physical data of **18** were in good agreement with those described for methyl 2,3-di-O-acetyl-4-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside by Bebault *et al.*[10]

The proposed α-L-configuration of the glycosidic bonds of **16**, **17**, and **18** was confirmed by detailed ^{13}C-NMR spectroscopy. The assigned values of C-1–H-1 and C-1′–H-1′ couplings are shown in Table 1.

Saponification of **16–18** gave, in almost quantitative yield, the unprotected methyl dirhamnosides (**19**, **20**, and **21**), respectively, as solid foams (isolated by lyophylisation), whereas the crystalline hexa-O-acetyldirhamnosides (**22–24**) were obtained on acetolysis. Saponification of the latter compounds led to the unsubstituted rhamnosyl-rhamnoses (**25–27**).

The ^{13}C-NMR spectroscopic studies of **25**, **26**, and **27** showed that, as expected, in aqueous solution these derivatives are present as anomeric mixtures at the reducing-end; however, in the case of **25** the ratio of the β-anomer was found to be less than 10%. The signal of the C-1′ carbon atom of **25** was doubled, with an intensity corresponding to the α/β ratio of the reducing-end, but the signals of C-2′–C-6′ were not doubled. This effect, characteristic for (1→2)-linked glycosyl-glycoses, was first reported by Usui *et al.*[28]

The above three disaccharide syntheses were carried out using similar intermediates, and this circumstance gave a possibility for performing comparative ^{13}C-NMR spectroscopy. It is well known that for models of the glycosylation shifts, the spectral data of monosaccharide methyl ethers are generally used,[29,30] despite the fact that the values of the methylation shift are higher by *ca* 3 ppm than those of the glycosylation shifts. Gorin[31] has shown that the values of the shifts of isopropyl ethers are closer to the values of glycosylation shifts than those of the methylation shifts.

Our earlier studies have shown that the benzyl ethers of monosaccharides are more suitable models for comparative ^{13}C-NMR investigations than the corresponding methyl ethers. For this purpose, the hitherto unknown methyl 2-O- (**28**) and 3-O-benzyl-α-L-rhamnopyranosides (**29**), methyl 4-O-benzyl-α-L-rhamnopyranoside (**30**) and the di-O-acetyl derivatives of the latter three compounds (**31–33**) were synthesised. Catalytic hydrogenation of **31–33** furnished methyl 3,4-di-O-acetyl- (**34**), methyl 2,4-di-O-acetyl- (**35**) and methyl 2,3-di-O-acetyl-α-L-rhamnopyranoside (**36**), respectively. Besides these model compounds the ^{13}C-NMR spectra of methyl 2,3,4-tri-O-benzyl-α-L-rhamnopyranoside (**37**),[32] methyl 2-O-methyl-3,4-di-O-benzyl- (**38**),[33] methyl 2,4-di-O-benzyl-3-O-methyl- (**39**),[33] methyl 2,3-di-O-benzyl-4-O-methyl- (**40**),[33] methyl 3,4-di-O-acetyl-2-O-methyl- (**41**),[34] methyl 2,4-di-O-acetyl-3-O-methyl- (**42**),[34] methyl 2,3-di-O-acetyl-4-O-methyl- (**43**),[34] methyl 2-O-methyl- (**44**),[34] methyl 3-O-methyl- (**45**)[34] and methyl 4-O-methyl-α-L-rhamnopyranoside (**46**)[34] were analysed in detail.

The tri-O-acetyl-rhamnosylation shifts could be defined comparing the spectra of **7**, **8** and **12** with that of

13–15; benzylation shifts were assigned analysing the spectra of 7, 8, 12 and 37, whereas the comparison of the spectra of 7, 8, 12 with that of 38–40 made it possible to introduce methylation shifts for the C-2–C-4 carbons, (while the two other C atoms of the methyl α-L-rhamnopyranoside were still benzylated).

Similarly, comparing the spectra of the methyl di-O-acetyl-α-L-rhamnopyranosides (34–36) with those of (16–18) and (31–33) and also with (41–43) the triacetyl-rhamnosylation shifts, the benzylation and methylation shifts were determined. The rhamnosylation shifts were obtained comparing of methyl α-L-rhamnopyranoside (47) with those of the methyl dirhamnosides (19–21). Benzylation and methylation shifts were determined analysing the spectra of compounds 28–30, and those of 44–46, respectively.

It may be concluded that the values of benzylation shifts are closer to the values of (triacetyl) rhamnosylation shifts than those of the methylation shifts, indicating that benzyl ethers are indeed more suitable model compounds for dirhamnosides, than the carbohydrate methyl ethers (Tables 2–4).

It is also to be noted that the values of chemical shifts of the branching C atoms of the methyl dirhamnoside peracetates 16 (C-2: 76.9 ppm), 17 (C-3: 75.1 ppm), 18 (C-4: 79.3 ppm) differ from each other in a significantly higher degree than the values observed for the corresponding C atom of the unsubstituted methyl dirhamnosides 19 (C-2: 77.8 ppm), 20 (C-3: 78.3 ppm) and 21 (C-4: 79.3 ppm).

This difference should be valuable for the ^{13}C-NMR spectroscopic studies of natural glycosides and oligosaccharides.

^{13}C–^{1}H inter-residue couplings in disaccharides may provide information about the orientation of the glycosidic bond ($^{3}J_{CH}$ values depend strongly on the dihedral angle). For our compounds, natural abundance, ^{1}H-coupled, ^{13}C-NMR spectra with 16 K data points permit to observe additional splitting of the C-1′ line with ^{3}J values of 4.6–5.6 Hz in case of acetylated rhamnobiosides (14: $^{3}J_{C_1\cdot H_2} = 4.6$ Hz, 17: $^{3}J_{C_1\cdot H_3} = 5.6$ Hz, 18: $^{3}J_{C_1\cdot H_4} = 4.8$ Hz). For the free sugars (25, 16, 27) the observed inter-residue couplings are less than 2 Hz. Assuming the Karplus-curve for the variation of ^{3}J with the torsional angle and taking the smaller angles of the two-valued representation, the above findings may be interpreted in such a way, that the parent disaccharides have an average dihedral angle corresponding to a staggered conformation, while in the acetylated derivatives this angle is near to the trans orientation ($\psi \sim 10°$). Similar interpretation and ^{3}J values were also reported[35] for maltose derivatives.

EXPERIMENTAL

General. M.ps were determined on a Kofler apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. ^{1}H- and ^{13}C-NMR spectra were taken at room temp and at the frequency of 100.1 or 25.16 MHz with VARIAN XL-100-FT-15 and JEOL MH-100 spectrometers, using TMS or dioxan as an internal reference. $^{1}J_{CH}$ coupling constants were determined from natural-abundance proton-coupled spectra measured by the gated decoupling technique.

Tlc was performed on Kieselgel G (Merck) using the solvent systems given in parentheses. Glc was carried out on a Hewlett–Packard 5830A instrument fitted with a helical stainless-steel column (4 ft × 0.2 mm i.d.) packed with 10% of UCW-982 Chromosorb WAW/DMCS (80–100 mesh). The temperature programme was started from 250° at 5°/min. The carrier gas was nitrogen at 20 ml/min.

Methyl 4-O-*acetyl*-*exo*-(1) *and* endo-2,3-O-*benzylidene*-α-L-*rhamnopyranoside* (2).

A mixture of methyl α-L-rhamnopyranoside (5 g), N,N-dimethylformamide (30 ml), α,α-dimethoxytoluene (5 g) and toluene-*p*-sulphonic acid (100 mg) was placed in an equipment similar to that described by Horton *et al.*, and the mixture was kept *in vacuo* at 70–75° for 2 h. It was then cooled, diluted with $CHCl_3$ (200 ml), extracted with sat $NaHCO_3$aq (2 × 50 ml), and washed with water (3 × 50 ml). The organic layer was dried (Na_2SO_4) and concentrated *in vacuo* to a syrup (8 g), containing the *exo* and *endo* isomers in a 1:1 ratio. The crude syrupy product was treated conventionally with pyridine (80 ml) and Ac_2O (80 ml) to give a mixture of 1 and 2, which was crystallised from EtOH (30 ml) to give pure 1 (2.1 g). Crystallisation of the residue obtained on concentration of the mother liquor from cyclohexane (18 ml) gave pure 2 (1.7 g). The remaining mother liquor was evaporated to dryness and applied to a Kieselgel G column (150 g, eluant: hexane-EtOAc 4:1) to obtain second crops of pure 1 (1.2 g) and 2 (1.2 g).

The overall yield of 1: 3.3 g (38.1%), m.p. 102°, $[\alpha]_D$ −24.6° (*c* 1.73, $CHCl_3$), R_f 0.47 (hexane-EtOAc 4:1), R_T 4.75 min.

^{1}H-NMR data: δ 7.50–7.20 (m, 5H, aromatic protons); 6.19 (s, 1H, Ph–CH); 5.01 (q, 1H, H-4, $J_{4,5} = 10$ Hz); 4.94 (d, 1H, H-1, $J_{1,2} = 1$ Hz); 4.47 (q, 1H, H-3, $J_{3,4} = 7.7$ Hz); 4.12 (dd, 1H, H-2, $J_{2,3} = 5.2$ Hz); 3.83 (m, 1H, H-5, $J_{5,6} = 6.3$ Hz); 3.37 (s, 3H, OCH_3); 2.10 (s, 3H, OAc); 1.22 (d, 3H, C_5–CH_3). (Found: C, 62.48; H, 6.64. Calc. for $C_{16}H_{20}O_6$: C, 62.32; H, 6.53%).

The overall yield of 2: 2.9 g (33.5%), m.p. 81–82°, $[\alpha]_D$ +30.0° (*c* 1.77, $CHCl_3$), R_f 0.39 (hexane-EtOAc 4:1); R_T 4.33 min.

^{1}H-NMR data: δ 7.60–7.30 (m, 5H, aromatic protons); 5.88 (s, 1H, Ph–CH), 4.99 (d, 1H, H-1, $J_{1,2} = 1$ Hz); 4.94 (dd, 1H, H-4, $J_{4,5} = 10.0$ Hz); 4.33 (dd, 1H, H-3, $J_{3,4} = 6.9$ Hz); 4.20 (dd, 1H, H-2, $J_{2,3} = 6.1$ Hz); 3.77 (m, 1H, H-5, $J_{5,6} = 6.3$ Hz); 3.38 (s, 3H, OCH_3); 2.07 (s, 3H, OAc); 1.18 (d, 3H, C_5–CH_3). (Found: C, 62.41; H, 6.58. for $C_{16}H_{20}O_6$: C, 62.32; H, 6.53%).

Methyl exo-2,3-O-*benzylidene*-α-L-*rhamnopyranoside* (3). A soln of 1 (3.5 g) in abs MeOH (50 ml) was treated with 1N methanolic NaOMe (0.2 ml). After being kept at room temp for 16 hr the mixture was neutralised with Amberlite IR-120 (H^+) resin and concentrated. The crystalline residue was recrystallised from MeOH to give 2.85 g (94.4%), m.p. 78°, $[\alpha]_D$-16.0° (*c* 0.57, $CHCl_3$), R_T: 3.73 min.

^{1}H-NMR data: δ 7.40–7.20 (m, 5H, aromatic protons); 6.12 (s, 1H, Ph–CH); 4.90 (d, 1H, H-1, $J_{1,2} = 0.6$ Hz); 4.38 (dd, 1H, H-3; $J_{3,4} = 6.6$ Hz); 4.08 (dd, 1H, H-2; $J_{2,3} = 5.5$ Hz); 3.69 (m, 1H, H-5; $J_{5,6} = 6.0$ Hz); 3.48 (dd, 1H, H-4; $J_{4,5} = 9.5$ Hz); 3.34 (s, 3H, OCH_3); 2.95 (s, 1H, OH); 1.31 (d, 3H, C_5–CH_3). (Found: C, 63.49; H, 6.68. Calc. for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81%).

Methyl endo-2,3-O-*benzylidene*-α-L-*rhamnopyranoside* (4). Compound 2 (1.50 g) was saponified in 30 ml MeOH as described for 3, to obtain syrupy 4 (1.16 g; 89.6%), $[\alpha]_D$ −23° (*c* 1.02, $CHCl_3$). R_T: 3.26 min.

^{1}H-NMR data: δ 7.40–7.20 p.p.m. (m, 5H, aromatic protons); 5.84 (s, 1H, Ph–CH); 4.94 (s, 1H, H-1); 4.24–4.08 (m, 2H, H-2,3); 3.78 (m, 1H, H-5); 3.50 (m, 1H, H-4); 3.26 (s, 3H, OCH_3); 2.92 (s, 1H, OH); 1.28 (d, 3H, C_5–CH_3). (Found: C, 63.56; H, 6.71. Calc. for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81%).

Methyl 4-O-*benzyl*-exo-2,3-O-*benzylidene*-α-L-*rhamnopyranoside* (5). Compound 3 (3.25 g) was benzylated with benzyl chloride (40 ml) in the presence of KOH (5 g) at 105° for 4 hr. The organic layer was then removed by decantation and the residue was washed with $CHCl_3$ and filtered. After addition of a small amount of $NaHCO_3$, the filtrate was steam distilled and the syrupy product crystallised on cooling. Recrystallisation from hexane gave 2.87 g (62.7%) of 5, m.p. 94–95°, $[\alpha]_D$ −68.2° (*c* 1.56, $CHCl_3$). Lit.[18] m.p. 96–97°, $[\alpha]_D$ −70° (*c* 1, $CHCl_3$).

The terms "methylation", "benzylation" or "(triacetyl) rhamnosylation shifts" denote the change in the chemical shift of a particular C atom on methylation, benzylation or (triacetyl) rhamnosylation of the OH group attached to it.

Table 1. ^{13}C-NMR chemical shifts and $^{1}J_{CH}$ coupling constants of compounds investigated

Carbon	Compound																	
	7[a]	13[a]	37[a]	38[a]	8[a]	14[a]	39[a]	12[a]	15[a]	40[a]	34[a]	16[a]	31[a]	41[a]	35[a]	17[a]	32[a]	42[a]	36[a]
C-1	100.5	100.0	99.5 /166.5/	98.7	98.3	98.5 /167/	99.2	99.3	99.0	99.4	100.9	99.8 /164/	99.1	98.9	98.6 /170/	98.7 /171/	99.0	99.0	98.8
C-2	68.6	76.0	75.4	78.2	78.9	78.1	75.0	74.6	74.7	75.5	69.4	76.9	76.1	78.7	72.8	71.2	68.7	68.3	70.3
C-3	80.2	79.9	80.3	80.2	71.7	78.5	82.2	80.0	78.9	80.1	72.1	70.8	71.8	71.9	68.2	75.1	74.9	77.2	72.2
C-4	80.2	80.3	80.6	80.6	82.2	80.9	80.5	71.9	80.2	82.7	71.7	71.5	71.7	71.8	74.7	72.8	72.7	72.8	70.9
C-5	67.4	68.2	68.1	68.0	67.3	68.3	67.9	68.6	67.2	68.1	66.3	67.2	66.5	66.6	66.1	67.4	66.5	66.6	68.7
C-6	18.0	18.0	18.1	18.0	18.1	18.1	18.1	17.8	18.5	18.0	17.5	17.6	17.6	17.6	17.4	17.5	17.5	17.5	17.6
C-1'		99.3				99.4 /174/			99.3			99.4 /172/				99.0 /173/			
C-2'		69.9				70.1			70.0			70.2				70.6			
C-3'		69.3				69.3			69.5			68.9				68.8			
C-4'		71.3				71.3			71.0			71.3				71.4			
C-5'		66.9				67.0			67.0			66.5				66.7			
C-6'		17.4				17.5			17.3			17.3				17.3			
OCH_3-1	54.6	54.6	54.6	54.5	54.6	54.6	54.4	54.6	54.6	54.6	55.0	55.0	54.8	54.9	55.0	55.0	54.9	55.0	54.9
OCH_3-2				59.2										59.4					
OCH_3-3							57.5											57.6	
OCH_3-4										60.8									
Ph-CH_2-2			72.9		73.1	72.5	72.9	72.7	72.7	72.9			73.3						
Ph-CH_2-3	72.0	72.5	72.2	72.2				71.7	71.6	72.3							71.4		
Ph-CH_2-4	75.2	75.3	75.2	75.2	74.8	75.3	74.7												

Table 1 (*Contd*).

Carbon	18[a]	33[a]	43[a]	x[b]	19[b]	28[a]	44[a]	20[b]	29[a]	45[a]	21[b]	30[a]	46[a]	25[b]	26[b]	27[b]
C-1	98.6	98.7	98.7	101.1	100.5	98.6	98.0	101.6	100.8	101.0	101.5	100.7	101.0	93.4	94.6	94.5
	/171/	/170/		/168/	/170.0/			/170.2/			/169.7/		/167/			/169.4/
C-2	70.4	70.6	70.5	71.0	79.0	78.5	80.8	71.0	68.1	67.2	71.2	71.3	71.4	79.9	71.1	71.3
C-3	71.8	71.9	71.7	71.8	70.9	71.7	71.6	78.8	80.0	81.6	71.2	71.7	71.3	70.9	78.5	71.5
C-4	79.3	79.1	80.5	73.0	73.1	73.7	73.6	72.2	71.8	71.5	80.4	81.7	83.4	73.2	72.4	80.7
C-5	67.5	67.7	67.7	68.2	69.2	68.2	68.3	69.4	68.1	68.2	67.6	67.2	67.4	69.1	69.2	67.3
C-6	18.2	18.0	17.9	17.5	17.7	17.7	17.6	17.8	17.7	17.7	18.3	18.0	18.0	17.6	17.5	18.3
C-1'	99.6				102.9			103.0			102.2			102.8	102.7	102.1
	/172/				/170.6/			/170.3/			/171.5/					/171.2/
C-2'	70.2				71.1			71.1			71.9			70.9	72.0	71.2
C-3'	69.0				70.9			70.8			71.1			70.6	71.0	71.2
C-4'	71.3				72.9			73.0			72.7			72.8	73.0	72.8
C-5'	66.9				69.7			69.6			69.9			69.8	69.7	70.0
C-6'	17.3				17.8			17.8			17.6			17.4	17.7	17.3
OCH_3-1	55.0	54.8	54.9	54.8	55.6	54.6	54.8	55.4	54.7	54.8	55.4	54.7	54.8			
OCH_3-2							59.0									
OCH_3-3										57.1						
OCH_3-4			60.3										60.5			
Ph-CH_2-2						73.1										
Ph-CH_2-3									71.7							
Ph-CH_2-4		74.9										74.9				

x = Methyl α-L-rhamnopyranoside. [a] Measured in $CDCl_3$ solution. [b] Measured in D_2O solution.

Table 2. Methylation, benzylation and triacetyl-α-L-rhamnosylation shifts in methyl di-O-benzyl-α-L-rhamnopyranosides

	$\Delta\delta_{OH-OCH_3}$	$\Delta\delta_{OH-OCH_2Ph}$	$\Delta\delta_{OH-[O-Rhap(OAc)_3]}$
C-2	9.6	6.8	7.4
C-3	10.5	8.6	6.8
C-4	10.8	8.7	8.3

Table 3. Methylation, benzylation and triacetyl-α-L-rhamnosylation shifts in methyl di-O-acetyl-α-L-rhamnopyranosides

	$\Delta\delta_{OH-OCH_3}$	$\Delta\delta_{OH-OCH_2Ph}$	$\Delta\delta_{OH-[O-Rhap(OAc)_3]}$
C-2	9.3	6.7	7.5
C-3	9.0	6.7	6.9
C-4	9.6	8.2	8.4

Table 4. Methylation, benzylation and α-L-rhamnosylation shifts in methyl α-L-rhamnopyranoside

	$\Delta\delta_{OH-OCH_3}$	$\Delta\delta_{OH-OCH_2Ph}$	$\Delta\delta_{OH-[O-Rhap]}$
C-2	9.8	7.5	8.0
C-3	10.3	8.7	7.5
C-4	10.3	8.6	7.3

^{1}H-NMR data: δ 7.60–7.30 (m, 10H, 2Ph); 6.05 (s, 1H, Ph–CH); 4.89 (d, 1H, H-1, $J_{1,2}$ = 1 Hz); 4.83 (q, 2H, Ph–CH_2); 4.58 (dd, 1H, H-3, $J_{3,4}$ = 6.9 Hz), 4.11 (dd, 1H, H-2, $J_{2,3}$ = 5.4 Hz); 3.74 (m, 1H, H-5, $J_{5,6}$ = 6.1 Hz); 3.35 (s, 3H, OCH_3); 3.33 (dd, 1H, H-4, $J_{4,5}$ = 9.7 Hz); 1.33 (d, 3H, C_5–CH_3).

Methyl 4 - O - *benzyl* - endo - 2,3 - O - *benzylidene* - α - L - *rhamnopyranoside* (**6**). Compound **4** (5 g) was treated with benzyl chloride (60 ml) and KOH (7.5 g) as described for **5**. The syrupy residue obtained by steam distillation was dissolved in $CHCl_3$ (200 ml), washed with water (3 × 50 ml), until neutral, dried (Na_2SO_4), and evaporated to give **6** (4.85 g; 72.5%), $[\alpha]_D$ −34° (*c* 1.50, $CHCl_3$).

^{1}H-NMR data: δ 7.35–7.20 (m, 10H, 2Ph); 5.90 (s, 1H, Ph–CH); 4.98 (d, 1H, H-1, $J_{1,2}$ = 1 Hz); 4.67 (q, 2H, Ph–CH_2); 4.39 (t, 1H, H-3, $J_{3,4}$ = 6.6 Hz); 4.20 (dd, 1H, H-2, $J_{2,3}$ = 6.3 Hz); 3.72 (m, 1H, H-5, $J_{5,6}$ = 6.2 Hz); 3.36 (s, 3H, OCH_3); 3.24 (dd, 1H, H-4, $J_{4,5}$ = 9.8 Hz); 1.26 (d, 3H, C_5–CH_3).

Methyl 3,4-*di*-O-*benzyl*-α-L-*rhamnopyranoside* (**7**). To a soln of **5** (5 g) in 1:1 CH_2Cl_2-ether (100 ml) were added LAH (1.7 g) and a soln of $AlCl_3$ (5.0 g) in ether (30 ml), and the mixture was heated under reflux for 10 min. It was then cooled and the excess reagent was decomposed with EtOAc (15 ml) and water (30 ml). The mixture was diluted with ether (100 ml) and the organic layer was decanted from $Al(OH)_3$.

This ppt was washed with ether (2 × 25 ml), and the combined organic layers were washed with water (2 × 30 ml), dried (Na_2SO_4) and concentrated. According to glc, the crude syrupy product (4.86 g; 97.2%) contained; **8** (1.2%, R_T 11.11 min) and **7** (98.8%, R_T 11.81 min). The mixture was purified by column chromatography (Kieselgel G 250 g, $CHCl_3$-acetone 9:1) to give pure **7**: $[\alpha]_D$-46.4° (*c* 1.72, $CHCl_3$), R_f 0.66 ($CHCl_3$-acetone 9:1).

^{1}H-NMR data: δ 7.50–7.20 (m, 10H, aromatic protons); 4.78 (q, 2H, Ph–CH_2); 4.68 (s, 1H, H-1); 4.64 (s, 2H, Ph–CH_2); 4.05–3.50 (m, 4H, H-2,3,4,5); 3.32 (s, 3H, OCH_3); 2.40 (b, 1H, OH); 1.28 (d, 3H, C_5–CH_3). (Found: C, 70.12; H, 7.26. Calc. for $C_{21}H_{26}O_5$: C, 70.36; H, 7.31%).

Methyl 2,4-*di*-O-*benzyl*-α-L-*rhamnopyranoside* (**8**). Compound **6** (5 g) was hydrogenolysed with LAH (1.7 g) and $AlCl_3$ (5 g) as described for **7**. The syrupy product (4.69 g; 93.8%) contained (glc) 95.6% of **8** (R_T 11.11 min) and 4.4% of **7** (R_T 11.81 min). For microanalytical measurements 1 g of the product was purified by column chromatography (Kieselgel G 45 g, $CHCl_3$-acetone 9:1). $[\alpha]_D$-17.7° (*c* 0.48, $CHCl_3$), R_f 0.80 ($CHCl_3$-acetone, 9:1).

^{1}H-NMR data: δ 7.50–7.20 (m, 10H, aromatic protons); 4.75 (q, 4H, 2 Ph–CH_2); 4.70 (s, 1H, H-1); 3.85–3.35 (m, 4H, H-2,3,4,5); 3.33 (s, 3H, OCH_3); 2.40 (b, 1H, OH); 1.34 (d, 3H, C_5–CH_3). (Found: C, 70.21; H, 7.19. Calc. for $C_{21}H_{26}O_5$: C, 70.36; H, 7.31%).

Methyl 4-O-*allyl*-2,3-O-*isopropylidene*-α-L-*rhamnopyranoside* (**9**). A mixture of methyl 2,3-O-isopropylidene-α-L-rhamnopyranoside (3.3 g), N,N-dimethylformamide (100 ml) and sodium hydride (1.44 g) was stirred for 1 hr. It was then cooled to 0° and treated with allyl bromide (5 ml) for 12 hr. The excess of sodium hydride was decomposed with MeOH, the soln was filtered, and the filtrate was concentrated. The residue was dissolved in $CHCl_3$ (100 ml), washed with water (5 × 50 ml), dried (Na_2SO_4), and concentrated to give a syrup, which was purified by column chromatography (150 g of Kieselgel G, $CHCl_3$-acetone 95:5), yield: 2.85 g (73%). $[\alpha]_D$ −40.8° (*c* 1.11, $CHCl_3$). R_f 0.70 (light petroleum-ethyl acetate 3:2). (Found: C, 60.32; H, 8.64. Calc. for $C_{13}H_{22}O_5$: C, 60.44; H, 8.58%).

Methyl 4 - O - *allyl* - α - L - *rhamnopyranoside* (**10**). To a soln of **9** (2.2 g) in 1:1 EtOH-water (50 ml) was added conc. H_2SO_4 (0.2 ml) and the mixture was boiled for 2 hr. It was neutralised with Dowex-4 (OH^-) resin, evaporated and chromatographed on a Kieselgel G column, using light petroleum-EtOAc 3:2 as the eluant, yield: 1.75 g (94.1%), $[\alpha]_D$-85.3° (*c* 0.57, $CHCl_3$), R_f 0.15 (light petroleum-EtOAc 3:2). (Found: C, 55.45; H, 8.19. Calc. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31%).

Methyl 4-O-*allyl*-2,3-*di*-O-*benzyl*-α-L-*rhamnopyranoside* (**11**). Compound **10** (1.5 g) was benzylated with benzyl chloride (8 ml) and KOH (2.0 g) for 24 hr at 105°. The syrupy product, obtained by the usual work-up, was chromatographed on a

Kieselgel G column (150 g), using 2:1 light petroleum-EtOAc as the eluant, to give pure syrupy **11** (2.2 g; 80.3%), $[\alpha]_D$-39.9° (*c* 0.8, $CHCl_3$), R_f 0.63 (light petroleum-EtOAc 2:1). (Found: C, 72.85; H, 7.68. Calc. for $C_{24}H_{30}O_5$: C, 72.33; H, 7.59%).

Methyl 2,3-*di*-O-*benzyl*-α-L-*rhamnopyranoside* (**12**). A mixture of **11** (1.8 g) and 10% Pd–C (500 mg) in 2:1:1 EtOH-AcOH-water (150 ml) was heated under reflux for 45 hr with stirring. After filtration, the solvents were removed by evaporation to yield a syrupy residue, which was purified by column chromatography (80 g of Kieselgel G; 3:2 light petroleum-EtOAc). 1.33 g (82.1%) of syrupy **12** $[\alpha]_D$ + 9.0° (*c* 1.2, $CHCl_3$), R_f 0.6 (light petroleum-EtOAc 3:2) was obtained. (Found C, 70.82; H, 7.42. Calc. for $C_{21}H_{26}O_5$: C, 70.36; H, 7.31%).

Methyl 3,4-*di*-O-*benzyl*-2-O-(2,3,4-*tri*-O-*acetyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranoside* (**13**). Compound **7** (1.7 g) was dissolved in abs benzene (100 ml) and nitromethane (100 ml) and the soln was evaporated at atmospheric pressure to half its volume. It was cooled to 45° and treated with $Hg(CN)_2$ (1.48 g) and α-acetobromo-L-rhamnose (2.02 g), and then stirred for 4 hr under anhydrous conditions. The mixture was diluted with $CHCl_3$ (50 ml), filtered, and concentrated. The residue was dissolved in $CHCl_3$ (100 ml), the mixture was filtered, and the filtrate was washed with 5% KIaq (3 × 30 ml) and water (5 × 50 ml). After drying over Na_2SO_4, the organic layer was concentrated to a syrupy residue which crystallised on standing. Recrystallisation from ether–light petroleum gave 2.85 g (95.3%), m.p. 124–126°, $[\alpha]_D$-38.4° (*c* 0.53, $CHCl_3$), R_f 0.78 (light petroleum-EtOAc 2:1). (Found: C, 63.10; H, 6.84. Calc. for $C_{33}H_{42}O_{12}$: C, 62.84; H, 6.71).

Methyl 2,4-*di*-O-*benzyl*-3-O-(2,3,4-*tri*-O-*acetyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranoside* (**14**). Compound **8** (5.3 g) was treated with α-acetobromo-L-rhamnose (6.36 g) for 12 hr in 1:1 abs benzene–nitromethane (400 ml) in the presence of $Hg(CN)_2$ (4.58 g) as described for **13**. The syrupy product was chromatographed on a Kieselgel G column (440 g), using 2:1 *n*-hexane-EtOAc as the eluant, yield: 7.35 g (78.8%), $[\alpha]_D$-46.1° (*c* 0.56, $CHCl_3$), R_f 0.81 (light petroleum-EtOAc 2:1). (Found: C, 63.02; H, 6.63. Calc. for $C_{33}H_{42}O_{12}$: C, 62.84; H, 6.7%).

Methyl 2,3-*di*-O-*benzyl*-4-O-(2,3,4-*tri*-O-*acetyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranoside* (**15**). Coupling of **12** (0.6 g) with α-acetobromo-L-rhamnose (0.71 g) was carried out in 1:1 benzene-nitromethane (50 ml) in the presence of $Hg(CN)_2$ (0.5 g) as described for **13**. The syrupy product was chromatographed on a Kieselgel G column (80 g) with 3:1 light petroleum-EtOAc mixture to obtain pure syrupy **15** (710 mg; 67.2%), $[\alpha]_D$-48.2 (*c* 1.10, $CHCl_3$). R_f 0.79 (light petroleum-EtOAc 2:1). (Found: C, 62.96 H, 6.58. Calc. for $C_{33}H_{42}O_{12}$: C, 62.84; H, 6.71%).

Methyl 3,4-*di*-O-*acetyl*-2-O-(2,3,4-*tri*-O-*acetyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranoside* (**16**). A mixture of **13** (3.0 g), 10% Pd–C (0.5 g) in EtOH (100 ml) was hydrogenated for 3 hr. The catalyst was filtered off, the filtrate was concentrated, and the residue was acetylated with Ac_2O (25 ml) in pyridine (25 ml) for 12 hr. The solid product crystallised from EtOH to give **16** (2.2 g; 86.5%), m.p. 151–152°, $[\alpha]_D$-44.8° (*c* 0.81, $CHCl_3$). R_f 0.66 (light petroleum-EtOAc 3:2). (Found: C, 52.05 H, 6.48. Calc. for $C_{23}H_{34}O_{14}$: C, 51.68; H, 6.41%).

Methyl 2,4-*di*-O-*acetyl*-3-O-(2,3,4-*tri*-O-*acetyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranoside* (**17**), yield: 4.38 g (80.1%), m.p. 135–136°, lit.[14] m.p. 125°; $[\alpha]_D$-43.6° (*c* 1.2, $CHCl_3$), lit.[14] $[\alpha]_D$-48° ($CHCl_3$), R_f 0.63 (light petroleum-EtOAc 3:2). (Found: C, 51.72; H, 6.47. Calc. for $C_{23}H_{34}O_{14}$: C, 51.68; H, 6.41%).

Methyl 2,3-*di*-O-*acetyl*-4-O-(2,3,4-*tri*-O-*acetyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranoside* (**18**), yield: 520 mg (84.2%), m.p. 180–181°, lit.[10] m.p. 182–183°; $[\alpha]_D$-52.6° (*c* 1.48, chloroform), lit.[10] $[\alpha]_D$-51.7° (*c* 2.3, $CHCl_3$). R_f 0.59 (light petroleum-EtOAc 3:2). (Found: C, 52.00; H, 6.62. Calc. for $C_{23}H_{34}O_{14}$: C, 51.68; H, 6.41%).

Methyl 2-O-α-L-*rhamnopyranosyl*-α-L-*rhamnopyranoside* (**19**). Compound **16** (1.2 g) was deacetylated with 0.1 M methanolic NaOMe (30 ml) for 2 hr. The soln was neutralised with Amberlite IR-120 (H^+) resin and on freeze-drying gave **19** (0.7 g; 96%) $[\alpha]_D$-92° (*c* 1.28, water); homogeneous on tlc R_f 0.21, (butanone-water azeotrope).

Methyl 3-O-α-L-*rhamnopyranosyl*-α-L-*rhamnopyranoside* (**20**). Compound **17** (2.0 g) was deacetylated as described for **19** to give syrupy **20** (1.15 g; 95%), $[\alpha]_D$-78° (*c* 1.52, water), R_f 0.23 (butanone-water azeotrope).

Methyl 4-O-α-L-*rhamnopyranosyl*-α-L-*rhamnopyranoside* (**21**). Compound **18** (0.5 g) was deacetylated as described for **19** to give syrupy **21** (0.27 g; 90%), $[\alpha]_D$-107.6° (*c* 1.52, water), lit.[10] $[\alpha]_D$-109° (*c* 2.5, water), R_f 0.20 (butanone–water azeotrope).

1,3,4-*Tri*-O-*acetyl*-2-O-(2,3,4-*tri*-O-*acetyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranose* (**22**). Following the description of Bebault *et al.*[10] for the preparation of **24**, compound **16** (1 g) and Ac_2O (6 ml) were shaken with 1% (v/v) conc H_2SO_4–Ac_2O (12 ml) for 2 hr at room temp. The mixture was poured with stirring into ice-water, containing $NaHCO_3$. The resulting syrup solidified on standing and the solid was recrystallised from EtOH to give pure **22** (0.65 g; 62%), m.p. 118–120°, $[\alpha]_D$ − 48° (*c* 1.5, $CHCl_3$). (Found: C, 51.38; H, 6.16. Calc. for $C_{24}H_{34}O_{15}$: C, 51.25; H, 6.09%).

1,2,4-*Tri*-O-*acetyl*-3-O-(2,3,4-*tri*-O-*acetyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranose* (**23**). Compound **17** (2.2 g) was acetolysed as described for **22**. The crude product solidified upon repeated treatment with ice-water, and it was recrystallised from EtOH to yield **23** (1.5 g; 64.9%), m.p. 75–76°, Lit.[14] syrup, $[\alpha]_D$ − 43.6° (*c* 0.51, $CHCl_3$), lit.[14] $[\alpha]_D$ − 32° (*c* 4.5, $CHCl_3$). (Found: C, 51.76; H, 6.18. Calc. for $C_{24}H_{34}O_{15}$: C, 51.25; H, 6.09%).

2-O-α-L-*Rhamnopyranosyl*-L-*rhamnose* (**25**). Compound **22** (0.4 g) was treated with NaOMe soln 0.1 M (10 ml) for 4 hr at room temp. After working up in the usual manner, the resulting syrup was dissolved in D_2O (2 ml) and freeze-dried to give a foam (186 mg; 84.3%), $[\alpha]_D$-26.2° (*c* 1.02, water). Lit.[13] $[\alpha]_D$-28.7°.

3-O-α-L-*Rhamnopyranosyl*-L-*rhamnose* (**26**). Compound **23** (1 g) was deactylated as described for **25**, syrup, (492 mg; 83.7%), $[\alpha]_D$-31° (*c* 1.05, water), lit.[14] $[\alpha]_D$-21° (*c* 3.2, water).

Methyl 2-O-*benzyl*-α-L-*rhamnopyranoside* (**28**). Compound **4** (0.5 g) was hydrogenolysed in CH_2Cl_2–ether (1:1) (40 ml) with LAH (140 mg) and $AlCl_3$ (0.5 g) at 40°, as described for **5**, to give a crude product, which was shown by TLC ($CHCl_3$–acetone 9:1) to consist of a major (R_f 0.21, R_T 7.91 min, 95%) and a minor component (R_f 0.33, R_T 8.43 min, 5%).

Purification of this mixture on a Kieselgel G column (30 g), using $CHCl_3$-acetone 9:1 as the eluant, gave syrupy **28** (0.41 g; 82%), $[\alpha]_D$ + 3.6 (*c* 0.59, $CHCl_3$). (Found: C, 62.86; H, 7.82. Calc. for $C_{14}H_{20}O_5$: C, 62.66; H, 7.51%).

Methyl 3-O-*benzyl*-α-L-*rhamnopyranoside* (**29**). Treatment of **3** (2 g) with the LAH–$AlCl_3$ reagent as described for **5** gave crude **29**. Recrystallisation from cyclohexane (120 ml) gave **29** (1.76 g; 88%), m.p. 92–94°, $[\alpha]_D$ − 25.3° (*c* 0.51, $CHCl_3$), R_f 0.33 ($CHCl_3$–acetone 9:1). (Found: C, 62.48; H, 7.58. Calc. for $C_{14}H_{20}O_5$: C, 62.66; H, 7.51%).

Methyl 3, 4-*di*-O-*acetyl*-2-O-*benzyl*-α-L-*rhamnopyranoside* (**31**). Conventional acetylation of **28** (0.15 g) resulted in syrupy **31** (186 mg; 94.4%), $[\alpha]_D$ − 21.1° (*c* 0.83, $CHCl_3$), R_f 0.26 (light petroleum-EtOAc 4:1), R_T 5.95 min.

^{1}H-NMR data: δ 7.40–7.20 (m, 5H, aromatic protons); 5.22–5.10 (m, 2H, H-3 and H-4); 4.60 (s, 3H, H-1 and Ph–CH_2); 3.78 (m, 2H, H-2 and H-5); 3.34 (s, 3H, OCH_3); 2.00 and 1.95 (2s, 6H, OAc-3,4); 1.21 (d, 3H, C_5–CH_3, $J_{5,6}$ = 6 Hz).

Methyl 2,4-*di*-O-*acetyl*-3-O-*benzyl*-α-L-*rhamnopyranoside* (**32**). Compound **29** (0.2 g) was conventionally acetylated to give syrupy **32** (230 mg; 87%), $[\alpha]_D$ − 6.7° (*c* 0.72, $CHCl_3$), R_f 0.24 (light petroleum-EtOAc 4:1), R_T 5.20 min.

^{1}H-NMR data: δ 7.40–7.20 (m, 5H, aromatic protons); 5.30 (dd, 1H, H-2; $J_{2,3}$ = 2.5 Hz); 5.14 (dd, 1H, H-4; $J_{4,5}$ = 10 Hz); 4.60 (d, 1H, H-1; $J_{1,2}$ = 1.5 Hz); 4.46 (q, 2H, Ph–CH_2); 3.80 (dd, 1H, H-3; $J_{3,4}$ = 9.5 Hz); 3.66 (m, 1H, H-5); 3.33 (s, 3H, OCH_3); 2.11 (s, 3H, OAc-4); 1.97 (s, 3H, OAc-2); 1.18 (d, 3H, C_5–CH_3, $J_{5,6}$ = 6 Hz).

Methyl 2,3-*di*-O-*acetyl*-4-O-*benzyl*-α-L-*rhamnopyranoside* (**33**). Compound **30** (1.2 g) was conventionally acetylated to give syrupy **33** (1.26 g; 80%), $[\alpha]_D$ − 39.4° (*c* 2.51, $CHCl_3$), R_f 0.23 (light petroleum-EtOAc 4:1), R_T 6.28 min.

Methyl 3,4-*di*-O-*acetyl*-α-L-*rhamnopyranoside* (**34**). Compound **31** (300 mg) was hydrogenated in the presence of PdC (100 mg) in EtOH (30 ml). After the usual work-up, the product was recrystallised from EtOAc-cyclohexane to give **34** (170 mg; 76%), m.p. 114–115°, $[\alpha]_D$ − 103° (*c* 1.1, $CHCl_3$), R_f: 0.72 (CH_2Cl_2-acetone 4:1).

^{1}H-NMR data: δ 5.22–5.00 (m, 2H, H-3,4); 4.72 (s, 1H, H-1); 4.08 (dd, 1H, H-2); 3.88 (m, 1H, H-5); 3.37 (s, 3H, OCH_3); 2.92 (b, 1H, OH); 2.05 and 2.01 (2s, 6H, OAc-3 and OAc-4); 1.20 (d, 3H, C_5–CH_3, $J_{5,6}$ = 6 Hz).

Methyl 2,4-di-O-acetyl-α-L-rhamnopyranoside (**35**). Treatment of **32** (700 mg) with PdC (150 mg) in EtOH (40 ml) resulted in **35** (440 mg; 84%), m.p. 100–101° (from ether-hexane), $[\alpha]_D$ −31.6° (*c* 1.29, $CHCl_3$). R_f 0.74 (CH_2Cl_2-acetone 4:1).

^{1}H-NMR data: δ 5.05 (dd, 1H, H-2; $J_{2,3}$ = 1.5 Hz); 4.86 (dd, 1H, H-4; $J_{4,5}$ = 10.5 Hz); 4.65 (s, 1H, H-1; $J_{1,2}$ = 1 Hz); 4.03 (dd, 1H, H-3; $J_{3,4}$ = 10.2 Hz); 3.92 (m, 1H, H-5; $J_{5,6}$ = 6 Hz); 3.34 (s, 3H, OCH_3); 2.84 (s, 1H, OH); 2.13 (s, 3H, OAc-4); 2.09 (s, 3H, OAc-2); 1.19 (d, 3H, C_5–CH_3).

Methyl 2, 3-di-O-acetyl-α-L-rhamnopyranoside (**36**). Compound **33** (1.5 g) was treated with Pd–C (200 mg) in EtOH (100 ml) to give **36** (1.02 g; 91%) as a syrup, $[\alpha]_D$ −39° (*c* 1.0, $CHCl_3$), R_f 0.76 (CH_2Cl_2-acetone 4:1).

^{1}H-NMR data: δ 5.20 (dd, 1H, H-2; $J_{2,3}$ = 3 Hz); 5.12 (dd, 1H, H-3; $J_{3,4}$ = 9 Hz); 4.59 (s, 1H, H-1); 3.68 (m, 2H, H-4,5); 3.37 (s, 3H, OCH_3); 2.58 (b, 1H, OH); 2.11 and 2.04 (2s, 6H, OAC-2,3); 1.35 (d, 3H, C_5–CH_3; $J_{5,6}$ = 6 Hz).

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