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SYNTHESIS AND HYDROGENOLYSIS OF THE METHYLENE, ETHYLIDENE, ISOPROPYLIDENE, AND DIASTEREOISOMERIC 1-PHENYLETHYLIDENE ACETALS OF β-L-ARABINO- AND α-L-RHAMNO-PYRANOSIDE DERIVATIVES

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ABSTRACT

Both diastereoisomers of 1-phenylethylidene acetals (acetophenone acetals) of methyl and benzyl β-L-arabinopyranoside and α-L-rhamnopyranoside were prepared. Acetal-exchange reactions gave only the *endo*-phenyl isomers; their 2-*O*- and 4-*O*-acetyl derivatives were isomerised into the *exo*-phenyl compounds. ^{1}H-N.m.r. data were used to determine the absolute configuration at the acetal carbon atom in these compounds. The protons of the methyl group of the *exo*-phenyl isomers resonate at lower field than those of the *endo*-phenyl isomers. Hydrogenolysis of various methylene, ethylidene, and isopropylidene derivatives gave *axial* ethers. The *endo*-phenyl isomers of the acetophenone derivatives also gave *axial* 1-phenylethyl ethers in two diastereoisomeric forms. The *exo*-phenyl isomers of the arabinosides were stable towards the reagent ($LiAlH_4$–$AlCl_3$), whereas the corresponding rhamnopyranosides gave the 2-(1-phenylethyl) ethers, but cleavage required prolonged reaction time and higher temperature.

INTRODUCTION

Bhattacharjee and Gorin[1,2] were the first to describe the reductive ring-cleavage reaction of carbohydrate acetals with the $LiAlH_4$–$AlCl_3$ reagent. Methylene, isopropylidene, propylidene, benzylidene, and cyclohexylidene acetals and cyclic orthoesters were investigated.

It was found later that the hydrogenolysis of dioxolane-type benzylidene derivatives is a highly stereoselective reaction, and that the direction of ring cleavage is determined by the orientation of the phenyl group[3,4]. Hitherto, it was not clear whether this stereoselectivity is due to the presence of the phenyl group *per se* or whether any suitably bulky group would suffice. Therefore, we have investigated the hydrogenolysis of various dioxolane-type acetal derivatives of pyranosides, namely methylene, ethylidene, isopropylidene, and acetophenone derivatives of methyl and benzyl β-L-arabinopyranside and α-L-rhamnopyranoside.

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RESULTS AND DISCUSSION

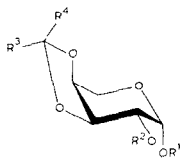
Apart from the methylene derivative **21**[5], all the acetals investigated were prepared by exchange reactions using 1,1-dimethoxyethane, 2,2-dimethoxypropane, and acetophenone dimethyl acetal and catalytic amounts of toluene-*p*-sulphonic acid.

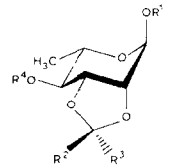
Oldham and Honeyman[6] showed that treatment of methyl β-L-arabinopyranoside with paraldehyde and sulphuric acid yielded diastereoisomeric ethylidene derivatives, to which Buchanan and Edgar[7] assigned structures on the basis of ^{1}H-n.m.r. spectra. Correlation of the ^{1}H-n.m.r. parameters with X-ray data[8] for the isomeric 3,4-*O*-ethylidenegalactopyranoside derivatives established the reliability of the ^{1}H-n.m.r. method. Buchanan and Edgar[7] observed the strong preference for the formation of the *endo*-methyl isomers.

Ethylidenation of benzyl β-L-arabinopyranoside gave a mixture of **1** and **2** which could not be fractionated by chromatography, but from which the *endo*-methyl isomer **2** crystallised. The ^{1}H-n.m.r. data indicated the presence of <5% of **1**; hence, **2** was acetylated to give **4** which was equilibrated using $AlCl_3$ as catalyst. The proportion of the *exo*-methyl isomer **3** did not exceed 10%, but **3** and **4** could be separated by column chromatography. Saponification of **3** then gave crystalline **1**. Conventional methylation of **1** and **2** gave the respective 2-methyl ethers (**5** and **6**). As found by Buchanan and Edgar[7], the methine protons in the CH_3CH groups resonated below δ 5.14 for the *endo*-methyl isomers, and above δ 5.49 for the *exo*-methyl isomers.

Most of the isopropylidene derivatives (**7**[9], **8**[10], **22**[11], **23**[12], **24**[13], and **25**[14]) investigated were known previously, and **9** and **10** were prepared by treatment of **8** with benzyl bromide or methyl iodide in *N*,*N*-dimethylformamide.

Recently, the synthesis of the acetophenone derivatives **28** and **29** was described and the structure of **28** was established by X-ray crystallography[15]. Thus, it was possible to correlate the ^{1}H- and ^{13}C-n.m.r. data with configuration at the acetal carbon atom; the chemical shifts of the signals of the methyl protons were





1 R^1 = Bzl, R^2 = R^4 = H, R^3 = CH_3
2 R^1 = Bzl, R^2 = R^3 = H, R^4 = CH_3
3 R^1 = Bzl, R^2 = Ac, R^3 = CH_3, R^4 = H
4 R^1 = Bzl, R^2 = Ac, R^3 = H, R^4 = CH_3
5 R^1 = Bzl, R^2 = R^3 = CH_3, R^4 = H
6 R^1 = Bzl, R^2 = R^4 = CH_3, R^3 = H
7 R = R^3 = R^4 = CH_3, R^2 = H
8 R = Bz., R^2 = H, R^3 = R^4 = CH_3
9 R^1 = R^2 = Bzl, R^3 = R^4 = CH_3
10 R^1 = Bzl, R^2 = R^3 = R^4 = CH_3

11 R^1 = R^4 = CH_3, R^2 = H, R^3 = Ph
12 R^1 = R^3 = CH_3, R^2 = H, R^4 = Ph
13 R^1 = R^4 = CH_3, R^2 = Ac, R^3 = Ph
14 R^1 = R^3 = CH_3, R^2 = Ac, R^4 = Ph
15 R = Bzl, R^2 = H, R^3 = Ph, R^4 = CH_3
16 R = Bzl, R^2 = H, R^3 = CH_3, R^4 = Ph
17 R^1 = Bzl, R^2 = Ac, R^3 = Ph, R^4 = CH_3
18 R^1 = Bz, R^2 = Ac, R^3 = CH_3, R^4 = Ph
19 R^1 = R^2 = Bzl, R^3 = Ph, R^4 = CH_3
20 R^1 = R^2 = Bzl, R^3 = CH_3, R^4 = Ph

21 R^1 = CH_3, R^2 = R^3 = H, R^4 = Bzl
22 R = R^2 = R^3 = CH_3, R^4 = H
23 R^1 = R^2 = R^3 = CH_3, R^4 = Bzl
24 R = Bzl, R^2 = R^3 = CH_3, R^4 = H
25 R^1 = R^4 = Bzl, R^2 = R^3 = CH_3
26 R = R^4 = CH_3, R^2 = Ph, R^4 = H
27 R^1 = R = CH_3, R^3 = Ph, R^4 = H
28 R^1 = R^4 = CH_3, R^2 = Ph, R^3 = Ac
29 R = R^2 = CH_3, R^3 = Ph, R^4 = Ac

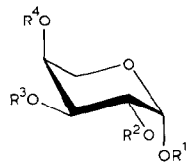
diagnostic, being to lower field for the *exo*-phenyl isomers than for the *endo*-phenyl isomers.

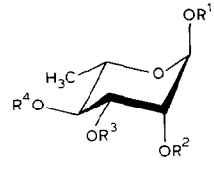
The reaction of methyl or benzyl β-L-arabinopyranoside and methyl α-L-rhamnopyranoside severally with acetophenone dimethyl acetal gave **12, 16,** and **27**, and isomerisation into the respective diastereoisomers did not occur under the reaction conditions used. On the other hand, the acetylated derivatives (**14, 18,** and **29**) of the kinetic products isomerised easily to give equilibrium mixtures of the diastereoisomers. The equilibrium ratio was determined only for the rhamnopyranosides and was 5:95 in favour of the *exo*-phenyl isomer **28**. Deacetylation of **13, 17,** and **28** gave the *exo*-phenyl diastereoisomers **11, 15,** and **26**, respectively.

Conventional benzylation of **15** and **16** produced **19** and **20**, respectively. The ^1H- and ^{13}C-n.m.r. data indicated the products of the acetal-exchange reaction to have the *endo*-phenyl configuration, which did not change during acetylation or benzylation. Isomerisation of the acetates gave *exo*-phenyl isomers.

endo-Phenyl isomers are also the kinetic products[16] in the formation of benzylidene acetals, and it seems likely that the *p*-methoxyacetophenone acetals prepared by Lipshutz and Morey[17] from methyl α-D-arabinopyranoside and methyl α-L-rhamnopyranoside, using *p*-methoxyacetophenone dimethyl acetal or α,*p*-dimethoxystyrene, also have the *endo*-*p*-methoxyphenyl structure. These authors could not isolate the other diastereoisomers.

Reductive ring-cleavage of the foregoing cyclic acetals was carried out using the $LiAlH_4$–$AlCl_3$ reagent. The hydrogenolysis of the 3,4-*O*-ethylidene derivative **6** gave 95% of benzyl 4-*O*-ethyl-2-*O*-methyl-β-L-arabinopyranoside (**30**), but **5** gave a 69:31 ratio of products (determined by g.l.c.), the major being benzyl 3-*O*-ethyl-2-*O*-methyl-β-L-arabinopyranoside with **30** as the minor product. These results are similar to those for 3,4-*O*-benzylidenearabinosides[19] and show that the selectivity of ring cleavage is not a function of the phenyl ring.





30 R^1 = Bzl, R^2 = CH_3, R^3 = H, R^4 = Et
33 R^1 = CH_3, R^2 = R^3 = H, R^4 = ^{i}Pr
34 R^1 = Bzl, R^2 = R^3 = H, R^4 = ^{i}Pr
35 R^1 = R^2 = Bzl, R^3 = H, R^4 = ^{i}Pr
36 R^1 = Bzl, R^2 = CH_3, R^3 = H, R^4 = ^{i}Pr
37 R^1 = CH_3, R^2 = R^4 = H, R^3 = ^{i}Pr
45 R^1 = CH_3, R^2 = R^3 = H, R^4 = CHPhCH$_3$ (*R*+*S*)
46 R^1 = R^2 = Bzl, R^3 = H, R^4 = CHPhCH$_3$ (*R*)
47 R^1 = R^2 = Bzl, R^3 = H, R^4 = CHPhCH$_3$ (*S*)

31 R^1 = R^2 = CH_3, R^3 = H, R^4 = Bzl
32 R^1 = R^3 = CH_3, R^2 = H, R^4 = Bzl
38 R^1 = CH_3, R^2 = ^{i}Pr, R^3 = R^4 = H
39 R^1 = CH_3, R^2 = ^{i}Pr, R^3 = H, R^4 = Bzl
40 R^1 = Bzl, R^2 = ^{i}Pr, R^3 = R^4 = H
41 R^1 = Bzl, R^2 = ^{i}Pr, R^3 = R^4 = Ac
42 R^1 = R^4 = Bzl, R^2 = ^{i}Pr, R^3 = H
43 R^1 = CH_3, R^2 = H, R^3 = ^{i}Pr, R^4 = Bzl
44 R^1 = R^4 = Bzl, R^2 = H, R^3 = ^{i}Pr
48 R^1 = CH_3, R^2 = CHPhCH$_3$ (*R*), R^3 = R^4 = H
49 R^1 = CH_3, R^2 = CHPhCH$_3$ (*S*), R^3 = R^4 = H

Reduction of the 2,3-*O*-methylene derivative **21**[5] required a prolonged reaction time. After 80 h, only 35% had reacted and 82% of the product mixture was methyl 4-*O*-benzyl-2-*O*-methyl-α-L-rhamnopyranoside[20] (**31**), the remainder being methyl 4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranoside[21] (**32**). Thus, attack of the reducing reagent at the equatorial oxygen of the rhamnoside **21** is preferred, and the major product had a structure similar to those obtained from *endo*-benzylidene isomers.

Similar results were also obtained with the isopropylidene derivatives. Thus, hydrogenolysis severally of **7**–**10** gave the 4-isopropyl ethers **33**–**36** in yields of 86, 82, 95, and 97%, respectively; the 3-isopropyl ether **37** was also isolated and characterised.

Likewise, the main products of the hydrogenolysis of the 2,3-*O*-isopropylidenerhamnopyranosides **22**–**25** were 2-isopropyl ethers, namely, **38** (96%), **39** (83%), **40** (99%), and **42** (68%). Only the minor products from **23** and **25** could be isolated, and were shown to be the 3-isopropyl ethers **43** (17%) and **44** (32%).

Hydrogenolysis of the 2-*O*-alkyl-L-arabinopyranosides **9** and **10** showed higher selectivity than for **7** and **8**, but, for L-rhamnopyranosides, compounds **22** and **24** having HO-4 unsubstituted gave 2-isopropyl ethers in high yield. A similar dependence was also found in the hydrogenolysis of benzylidene derivatives.

The hydrogenolysis of the acetophenone derivatives gave unexpected results. Thus, the *exo*-phenyl isomers of methyl 3,4-*O*-(1-phenylethylidene)-β-L-arabinopyranoside (**11**) and benzyl 2-*O*-benzyl-3,4-*O*-(1-phenylethylidene)-β-L-arabinopyranoside (**19**) were resistant towards the $LiAlH_4$–$AlCl_3$ reagent even at 45° for 8 h. However, at the same time, hydrogenolysis of the corresponding *endo*-phenyl isomers **12** and **20** was complete within 30 min at room temperature, to give methyl 4-*O*-(1-phenylethyl)-β-L-arabinopyranoside (**45**) and benzyl 2-*O*-benzyl-4-*O*-(1-phenylethyl)-β-L-arabinopyranoside (**46** and **47**). G.l.c. showed **45** to be a 1:1 mixture of diastereoisomers which could not be fractionated by t.l.c. Compounds **46** and **47** were isolated crystalline after chromatography and, on the basis of their optical rotations, the *R* and *S* configurations were assigned to **46** and **47**, respectively. The structure of **45** was established by the consumption of 1 mol of periodate. The ^{1}H-n.m.r. spectra of **46** and **47** contained one-proton multiplets (δ 3.95 and 4.08, respectively) which were changed to a doublet of doublets ($J_{2,3}$ 9.6, $J_{3,4}$ 3.6 Hz) for each compound on the addition of D_2O, showing that these protons were attached to carbon atoms having geminal OH groups. Thus, the 1-phenylethyl group must be at position 4 in **46** and **47**. This assumption was verified by methylation of **46** and **47**, and hydrogenolysis (Pd/C) of the products, which gave 3-*O*-methyl-L-arabinose[22]. This experiment showed that the 1-phenylethyl ether group can be cleaved under mild conditions.

The ring cleavage of the *endo*-phenyl isomer (**27**) of methyl 2,3-*O*-(1-phenylethylidene)-α-L-rhamnopyranoside proceeded smoothly and gave the 2-(1-phenylethyl) ethers **48** and **49** each of which could be oxidised by periodic acid,

showing that HO-3,4 were unsubstituted. Similar conclusions followed from inspection of the ^{13}C-n.m.r. data, since alkylation of HO-2 in α-L-rhamnopyranosides causes[23] a negative β-shift of 2.5 p.p.m.; C-1 in **48** and **49** resonated at 98.3 p.p.m.

The *exo*-phenyl isomer (**26**) of methyl 2,3-*O*-1-phenylethylidene-α-L-rhamnopyranoside reacted slowly with the $LiAlH_4$–$AlCl_3$ reagent even at higher temperature, and ring-cleavage was complete only after 8 h to give **48** and **49**. It is possible that **26** isomerised[18] slowly to **27** which reacted rapidly to give **48** and **49**, or, alternatively, **26** was slowly attacked at O-3. The former alternative is preferred.

Since diastereoisomers were formed on hydrogenolysis of the acetophenone derivatives, it is assumed that formation of the intermediate oxocarbonium ion[24] is faster than its reduction by hydride ion, so that the reducing agent can attack either face of the oxocarbonium ion. This contrasts with the 4,6-*O*-(1-phenylethylidene) derivatives, where the rate of the reduction is greater than that of the formation of the oxocarbonium ion, and only one of the two theoretically possible diastereoisomers is formed[25].

The hydrogenolysis of dioxolane-type ketal derivatives offers a new route for the preparation of *axial*-ethers of carbohydrates, and the products from the acetophenone derivatives contain an ether bond which is readily cleaved. The only disadvantage of these latter derivatives is that they are produced as mixtures of diastereoisomers.

EXPERIMENTAL

Melting points were determined on a Kofler apparatus and are uncorrected. Optical rotations were determined with a Perkin–Elmer 241 polarimeter. N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Bruker WP-200 spectrometer at room temperature. T.l.c. was performed on Kieselgel 60 F_{254} (Merck) with detection by charring with sulphuric acid. G.l.c. was performed using a Hewlett–Packard 5840A instrument with nitrogen as the carrier gas, generally at 20 mL/min. The temperature of the injector was 200°, and that of the flame-ionisation detector was 300°. The following columns were used: stainless steel (1.2 m × 2 mm i.d.) packed with 10% of UCW-982 on Gas Chrom Q (80–100 mesh) at (*a*) 180°; (*b*) 150°, then +5°/min; (*c*) 1 min at 225°, then +5°/min; (*d*) 240°; (*e*) 200°; nickel (0.5 m × 2 mm i.d.) packed with 10% of UCW-982 on Gas Chrom Q (80–100 mesh) at (*f*) 170°, then +5°/min; stainless steel (1.8 m × 2 mm i.d.) packed with OV-17 on Gas Chrom Q (80–100 mesh) at (*g*) 150° for 2 min, then +5°/min; OV-1 glass-capillary column (20 m × 0.3 mm i.d.), with nitrogen as carrier gas at 2 mL/min and at (*i*) 200°; (*j*) 190°; (*k*) 200° for 2 min, then +5°/min; (*l*) 180° for 2 min, then +2°/min.

Benzyl 3,4-O-(S)-ethylidene-β-L-arabinopyranoside (**2**). — A solution of benzyl β-L-arabinopyranoside[26] (5 g) in *N,N*-dimethylformamide (30 mL) was treated with 1,1-dimethoxyethane (10 mL) in the presence of toluene-*p*-sulphonic acid (0.1 g) *in vacuo* for 1 h at 40°. The cooled mixture was diluted with dichloromethane

(150 mL), washed with aqueous 5% $NaHCO_3$ (2 × 20 mL) and water (2 × 20 mL), dried (Na_2SO_4), and concentrated. The solid product was crystallised from hexane, to give the *endo*-ethyl isomer **2** (4.35 g, 78.2%), m.p. 104–106°, $[\alpha]_D$ +195° (*c* 1.4, chloroform), R_F 0.51 (dichloromethane–ethyl acetate, 4:1). ^{1}H-N.m.r. data: δ 7.50–7.15 (m, 5 H, Ph), 5.12 (q, 1 H, MeC*H*), 4.91 (d, 1 H, H-1), 4.66 (q, 2 H, PhCH_2), 4.16 (t, 1 H, H-3), 4.13–3.90 (m, 3 H, H-4,5,5'), 3.73 (m, 1 H, H-2), 2.50 (d, 1 H, OH), 1.42 (d, 3 H, *Me*CH); $J_{1,2}$ 3.7, $J_{2,3}$ 5.8, $J_{3,4}$ 5.8, $J_{H,OH}$ 8, $J_{CH,Me}$ 4.9 Hz. After the addition of D_2O, the d at δ 2.50 disappeared and the m at δ 3.73 collapsed to a dd.

Anal. Calc. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.19; H, 6.86.

*Benzyl 2-O-acetyl-3,4-O-(*R*)-* (**3**) *and 3,4-O-(*S*)-ethylidene-β-*L*-arabinopyranoside* (**4**). — Compound **2** (2.8 g) was acetylated in pyridine (30 mL) with acetic anhydride (30 mL) for 16 h at room temperature, to give a syrupy product which was dissolved in dichloromethane (150 mL) and isomerised by adding $AlCl_3$ (0.20 g) in ether (5 mL). The solution was stored for 48 h at 20°, washed with aqueous 5% $NaHCO_3$ (2 × 20 mL) and water (3 × 20 mL), dried (Na_2SO_4), and concentrated. T.l.c. of the residue then detected two components with R_F 0.27 and 0.22 (light petroleum–ethyl acetate, 4:1). The product (3 g) was fractionated by column chromatography to give, first, the syrupy *exo*-3,4-*O*-ethylidene derivative **3** (0.15 g, 4.6%), $[\alpha]_D$ +188° (*c* 0.7, chloroform), R_F 0.27. ^{1}H-N.m.r. data: δ 7.50–7.20 (m, 5 H, Ph), 5.49 (q, 1 H, MeC*H*), 5.14–4.83 (m, 2 H, H-1,2), 4.67 (q, 2 H, PhCH_2), 4.56 (t, 1 H, H-4), 4.03 (m, 2 H, H-5,5'), 2.13 (s, 3 H, OAc), 1.40 (d, 3 H, *Me*CH).

Anal. Calc. for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.39; H, 6.60.

Eluted second was the syrupy *endo*-3,4-*O*-ethylidene derivative **4** (2.02 g, 62.5%), $[\alpha]_D$ +254° (*c* 1.4, chloroform), R_F 0.22. ^{1}H-N.m.r. data: δ 7.40–7.15 (m, 5 H, Ph), 5.15 (q, 1 H, MeC*H*), 5.01 (d, 1 H, H-1), 4.81 (dd, 1 H, H-2), 4.60 (q, 2 H, PhCH_2), 4.34 (dd, 1 H, H-3), 4.18–3.99 (m, 3 H, H-4,5,5'), 2.05 (s, 3 H, OAc), 1.43 (d, 3 H, *Me*CH); $J_{1,2}$ 3.5, $J_{2,3}$ 8.1, $J_{3,4}$ 5.6, $J_{CH,Me}$ 5.3 Hz.

Anal. Found: C, 62.30; H, 6.59.

*Benzyl 3,4-*O*-(*R*)-ethylidene-β-*L*-arabinopyranoside* (**1**). — Compound **3** (0.1 g) was deacetylated in methanol (3 mL) with NaOMe (0.005 g), to give the *exo*-ethyl isomer **1** (0.08 g, 92.3%), m.p. 100–102° (from ethanol), $[\alpha]_D$ +201° (*c* 0.5, chloroform), R_F 0.51 (dichloromethane–ethyl acetate, 4:1). ^{1}H-N.m.r. data: δ 7.55–7.30 (m, 5 H, Ph), 5.45 (q, 1 H, CH_3C*H*), 4.95 (d, 1 H, H-1), 4.66 (q, 2 H, PhCH_2), 4.28 (dd, 1 H, H-3), 4.18–4.13 (m, 1 H, H-4), 3.95 (d, 2 H, H-5,5'), 3.77 (ddd, 1 H, H-2), 2.27 (d, 1 H, OH), 1.35 (d, 3 H, *Me*CH); $J_{1,2}$ 3.7, $J_{2,3}$ 7.2, $J_{3,4}$ 5.5 Hz, $J_{CH,Me}$ 4.8 Hz.

Anal. Calc. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.30; H, 6.77.

*Benzyl 3,4-*O*-(*R*)-ethylidene-2-*O*-methyl-β-*L*-arabinopyranoside* (**5**). — A solution of **1** (0.05 g) in *N*,*N*-dimethylformamide (3 mL) was treated with methyl iodide (0.5 mL) in the presence of silver oxide (0.50 g). After 24 h, the mixture was worked-up, to give the syrupy *exo*-ethyl isomer **5** (0.048 g, 91%), $[\alpha]_D$ +187° (*c* 0.35, chloroform), R_F 0.62 (dichloromethane–ethyl acetate, 4:1).

Anal. Calc. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.30; H, 7.14.

Benzyl 3,4-O-(S)-ethylidene-2-O-methyl-β-L-arabinopyranoside (**6**). — A solution of **2** (0.720 g) in *N,N*-dimethylformamide (10 mL) was methylated with methyl iodide (0.51 mL) in the presence of NaH (0.2 g) for 30 min[28]. The mixture was worked-up, to give the syrupy *endo*-ethyl isomer **6** (0.729 g, 96.5%), $[\alpha]_D$ +211° (*c* 1.8, chloroform), R_F 0.62 (light petroleum–ethyl acetate, 7:3). ^{1}H-N.m.r. data: δ 7.40–7.15 (m, 5 H, Ph), 5.07 (q, 1 H, MeC*H*), 4.90 (d, 1 H, H-1), 4.59 (q, 2 H, PhCH_2), 4.34–3.82 (m, 5 H, skeleton protons), 3.36 (s, 3 H, OMe), 1.41 (d, 3 H, *Me*CH).

Anal. Calc. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.32; H, 7.23.

Benzyl 2-O-benzyl-3,4-O-isopropylidene-β-L-arabinopyranoside (**9**). — A mixture of **8**[10] (0.5 g), powdered KOH (1 g), and benzyl chloride (4 mL) was kept at 100° for 4 h, cooled, and washed with water (2 × 5 mL). The benzyl chloride was removed by steam distillation, and the oily residue was purified on a column of Kieselgel G (15 g) with light petroleum–ethyl acetate (7:3), to give syrupy **9** (0.495 g, 74.9%), $[\alpha]_D$ +165.5° (*c* 1.8, chloroform). ^{1}H-N.m.r. data: δ 7.40–7.10 (m, 10 H, 2 Ph), 4.80 (d, 1 H, H-1), 3.49 (dd, 1 H, H-2), 1.37 and 1.30 (2 s, 6 H, CMe_2).

Anal. Calc. for $C_{22}H_{26}O_5$: C, 71.33; H, 7.07. Found: C, 71.37; H, 7.11.

Benzyl 3,4-O-isopropylidene-2-O-methyl-β-L-arabinopyranoside (**10**). — Benzyl 3,4-*O*-isopropylidene-β-L-arabinopyranoside[10] (**8**, 2.18 g) was methylated in *N,N*-dimethylformamide (10 mL), using powdered KOH (1.8 g) and methyl iodide (1.2 mL), to give syrupy **10** (2.08 g, 90.8%), $[\alpha]_D$ +202° (*c* 0.5, chloroform). ^{1}H-N.m.r. data: δ 7.45–7.20 (m, 5 H, Ph), 4.98 (d, 1 H, H-1), 4.66 (q, 2 H, PhCH_2), 4.34–4.18 (m, 2 H, H-3,4), 3.96 (d, 2 H, H-5,5'), 3.44 (s, 3 H, OMe), 3.37 (dd, 1 H, H-2), 1.57 and 1.37 (2 s, 6 H, CMe_2); $J_{1,2}$ 3.2, $J_{2,3}$ 7.6, $J_{4,5} = J_{4,5'} = 2$ Hz.

Anal. Calc. for $C_{16}H_{22}O_5$: C, 65.29; H, 7.73. Found: C, 65.42; H, 7.68.

Methyl 2-O-acetyl-3,4-O-(S)-(1-phenylethylidene)-β-L-arabinopyranoside (**14**). — A solution of methyl β-L-arabinopyranoside[6] (2.25 g) in *N,N*-dimethylformamide (30 mL) was stirred with acetophenone dimethyl acetal (5 g) and toluene-*p*-sulphonic acid (0.14 g) *in vacuo* for 16 h at 70°. Work-up, as described for **2**, gave a crude product (3.5 g, 96%) which was treated with pyridine (15 mL) and acetic anhydride (15 mL) for 12 h at room temperature. The usual work-up gave a crystalline product (4 g) which contained (g.l.c.) 95% of the *endo*-phenyl isomer **14** and 5% of the *exo*-phenyl isomer **13**. The mixture was crystallised from hexane, to give **14** (2.67 g, 65.9%), m.p. 108–110°, $[\alpha]_D$ +156° (*c* 0.8, chloroform), R_F 0.71 (light petroleum–ethyl acetate, 6:4), *T* 7.85 min [column (*a*)]. ^{1}H-N.m.r. data: δ 4.69 (d, 1 H, H-1), 3.28 (s, 3 H, OMe), 2.00 (s, 3 H, OAc), 1.58 (s, 3 H, CMe).

Anal. Calc. for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.38; H, 6.57.

Methyl 2-O-acetyl-3,4-O-(R)-(1-phenylethylidene)-β-L-arabinopyranoside (**13**). — A solution of **14** (1.50 g) in dichloromethane (25 mL) was isomerised by treatment with a solution of $AlCl_3$ (0.1 g) in ether (5 mL) for 5 h at 20°. Work-up, as described for **3**, gave a syrup (1.45 g, 97%), which was fractionated by column chromatography (light petroleum–ethyl acetate, 6:4), to give the *endo*-phenyl

isomer **14** (0.2 g) and the *exo*-phenyl isomer **13** (0.8 g) as a syrup, $[\alpha]_D$ +111° (*c* 0.6, chloroform), R_F 0.78, *T* 9.11 min [column (*a*)]. ^{1}H-N.m.r. data: δ 4.86 (d, 1 H, H-1), 3.30 (s, 3 H, OMe), 2.12 (s, 3 H, OAc), 1.70 (s, 3 H, CMe).

Anal. Calc. for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.29; H, 6.52.

*Methyl 3,4-O-(*R*)-(1-phenylethylidene)-β-*L*-arabinopyranoside* (**11**). — Compound **13** (1.0 g) was deacetylated as described for the preparation of **1**, to give the *exo*-phenyl isomer **11** (0.85 g, 99%) as a syrup, $[\alpha]_D$ +124° (*c* 0.7, chloroform), R_F 0.47 (light petroleum–ethyl acetate, 6:4). ^{1}H-N.m.r. data: δ 4.78 (d, 1 H, H-1), 3.40 (s, 3 H, OMe), 2.40 (bs, 1 H, OH), 1.73 (s, 3 H, CMe).

Anal. Calc. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.17; H, 6.84.

*Methyl 3,4-O-(S)-(1-phenylethylidene)-β-*L*-arabinopyranoside* (**12**). — Compound **14** (1.0 g) was deacetylated as described for the preparation of **1**, to give the *endo*-phenyl isomer **12** (0.8 g, 93%) as a syrup, $[\alpha]_D$ +130° (*c* 0.7, chloroform), R_F 0.45 (light petroleum–ethyl acetate, 6:4). ^{1}H-N.m.r. data: δ 4.52 (d, 1 H, H-1), 3.32 (s, 3 H, OMe), 2.40 (bs, 1 H, OH), 1.56 (s, 3 H, CMe).

Anal. Calc. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.10; H, 6.83.

*Benzyl 3,4-O-(S)-(1-phenylethylidene)-β-*L*-arabinopyranoside* (**16**). — A solution of benzyl β-L-arabinopyranoside[26] (2.80 g) in *N,N*-dimethylformamide (20 mL) was treated with acetophenone dimethyl acetal (8 mL) in the presence of toluene-*p*-sulphonic acid (0.1 g) *in vacuo* for 2 h at 60°. The solution was then diluted with dichloromethane (150 mL), washed with aqueous 5% $NaHCO_3$ (2 × 20 mL) and water (2 × 20 mL), dried (Na_2SO_4), and concentrated. The crude product (4.4 g) was purified on a column of Kieselgel G (250 g) with dichloromethane–ethyl acetate (95:5), to give the syrupy *endo*-phenyl isomer **16** (3.36 g, 84.2%), $[\alpha]_D$ +158° (*c* 0.72, chloroform), R_F 0.53. ^{1}H-N.m.r. data: δ 7.70–7.15 (m, 10 H, 2 Ph), 4.72 (d, 1 H, H-1), 4.59 (q, 2 H, PhCH_2), 4.38–4.29 (m, 2 H, H-3,4), 3.96 (m, 2 H, H-5,5′), 3.47 (m, 1 H, H-2), 2.29 (d, 1 H, OH), 1.61 (s, 3 H, CMe); $J_{1,2}$ 3.9, $J_{2,3}$ 7.0 Hz.

Anal. Calc. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.40; H, 6.70.

*Benzyl 2-O-acetyl-3,4-O-(S)-(1-phenylethylidene)-β-*L*-arabinopyranoside* (**18**). — A solution of **16** (2.0 g) in pyridine (20 mL) was acetylated with acetic anhydride (20 mL), to give the syrupy *endo*-phenyl isomer **18** (2.11 g, 93.7%), $[\alpha]_D$ +190° (*c* 0.6, chloroform), R_F 0.32 (light petroleum–ethyl acetate, 4:1). ^{1}H-N.m.r. data: δ 7.55–7.10 (m, 10 H, 2 Ph), 4.88 (d, 1 H, H-1), 4.52 (q, 2 H, PhCH_2), 4.46–4.32 (m, 3 H, H-2,3,4), 4.02 (m, 2 H, H-5,5′), 1.98 (s, 3 H, OAc), 1.61 (s, 3 H, CMe).

Anal. Calc. for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29. Found: C, 69.00; H, 6.35.

*Benzyl 2-O-acetyl-3,4-O-(R)-(1-phenylethylidene)-β-*L*-arabinopyranoside* (**17**). — A solution of **18** (1.75 g) in dichloromethane (50 mL) was isomerised by treatment with $AlCl_3$ (0.2 g) for 3 h at room temperature. The solution was diluted with dichloromethane (50 mL), washed with aqueous 5% $NaHCO_3$ (3 × 15 mL) and water (2 × 15 mL), dried (Na_2SO_4), and concentrated. The syrupy residue (1.71 g) contained a 1:1 mixture of the *exo*- (**17**) and *endo*-phenyl isomer **18**.

Column chromatography of the mixture on Kieselgel G (150 g), using light petroleum–ethyl acetate (4:1), gave **17** (0.718 g, 41%), m.p. 104–106° (from cyclohexane), $[\alpha]_D$ +141° (*c* 2.27, chloroform), R_F 0.37. ^{1}H-N.m.r. data: δ 7.55–7.10 (m, 10 H, 2 Ph), 5.12–4.97 (m, 2 H, H-1), 4.59 (q, 2 H, PhCH_2), 4.39 (dd, 1 H, H-3), 4.03–3.79 (m, 3 H, H-4,5,5'), 2.04 (s, 3 H, OAc), 1.69 (s, 3 H, CMe).

Anal. Calc. for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29. Found: C, 68.90; H, 6.36.

The second component was **18** (0.62 g, 35.4%).

*Benzyl 3,4-O-(R)-(1-phenylethylidene)-β-*L*-arabinopyranoside* (**15**). — Compound **17** (0.50 g) was deacetylated with NaOMe (0.01 g) in methanol (50 mL), to give the *exo*-phenyl isomer **15** (0.435 g, 97.7%), m.p. 92–94° (from hexane), $[\alpha]_D$ +114° (*c* 0.96, chloroform), R_F 0.45 (dichloromethane–ethyl acetate, 95:5). ^{1}H-N.m.r. data: δ 7.60–7.10 (m, 10, 2 Ph), 4.96 (d, 1 H, H-1), 4.66 (q, 2 H, PhCH_2), 4.17 (t, 1 H, H-3), 4.04–3.76 (m, 4 H, H-2,4,5,5'), 2.88 (s, 1 H, OH), 1.71 (s, 3 H, CMe); $J_{1,2}$ 4.0, $J_{2,3}$ 6.4, $J_{3,4}$ 6.4 Hz.

Anal. Calc. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.84. Found: C, 70.28; H, 6.71.

*Benzyl 2-O-benzyl-3,4-O-(R)-(1-phenylethylidene)-β-*L*-arabinopyranoside* (**19**). — Compound **15** (0.22 g) was treated with benzyl bromide (2.5 mL) in the presence of KOH (0.44 g) for 5 h at 50°. The reaction mixture was diluted with dichloromethane (30 mL) and filtered, and benzyl bromide was removed by steam distillation. The oily residue was purified on a column of Kieselgel G (20 g), using light petroleum–ethyl acetate (2:1), to give the syrupy *exo*-phenyl isomer **19** (0.235 g, 84.6%), $[\alpha]_D$ +90° (*c* 0.8, chloroform), R_F 0.64. ^{1}H-N.m.r. data: δ 7.55–7.10 (m, 15 H, 3 Ph), 4.90 (d, 1 H, H-1), 4.75 and 4.58 (2 q, 4 H, 2 PhCH_2), 4.40 (dd, 1 H, H-3), 3.94–3.81 (m, 3 H, H-4,5,5'), 3.67 (dd, 1 H, H-2), 1.64 (s, 3 H, CMe); $J_{1,2}$ 3.4, $J_{2,3}$ 8.0, $J_{3,4}$ 5.8 Hz.

Anal. Calc. for $C_{27}H_{28}O_5$: C, 74.98; H, 6.53. Found: C, 75.06; H, 6.49.

*Benzyl 2-O-benzyl-3,4-O-(S)-(1-phenylethylidene)-β-*L*-arabinopyranoside* (**20**). — Compound **16** (1.21 g) was benzylated with benzyl bromide (12 mL) in the presence of KOH (2.42 g), as described for the preparation of **19**. The oily residue was purified on a column of Kieselgel G (150 g), using light petroleum–ethyl acetate (2:1), to give the syrupy *endo*-phenyl isomer **20** (1.30 g, 85.1%), $[\alpha]_D$ +156° (*c* 0.6, chloroform), R_F 0.58. ^{1}H-N.m.r. data: δ 7.65–6.90 (m, 15 H, 3 Ph), 4.74–4.08 (m, 7 H, H-1,3,4 and 2 PhCH_2), 3.98 (m, 2 H, H-5,5'), 3.22 (dd, 1 H, H-2), 1.62 (s, 3 H, CMe); $J_{1,2}$ 3.5, $J_{2,3}$ 8.2 Hz.

Anal. Calc. for $C_{27}H_{28}O_5$: C, 74.98; H, 6.53. Found: C, 75.10; H, 6.61.

*Methyl 4-O-acetyl-2,3-O-(R)-(1-phenylethylidene)-α-*L*-rhamnopyranoside* (**29**). — A solution of methyl α-L-rhamnopyranoside[27] (15 g) in *N,N*-dimethylformamide (135 mL) was stirred with acetophenone dimethyl acetal (29.56 g) and toluene-*p*-sulphonic acid (0.432 g) *in vacuo* for 20 h at 75°. After work-up as described for **2**, the resulting syrup was treated with pyridine (100 mL) and acetic anhydride (100 mL) for 12 h at room temperature. The usual work-up gave a syrupy product (17.0 g, 87.5%), which contained [g.l.c., column (*b*)] 97% of the *endo*-phenyl isomer **29** and 3% of the *exo*-phenyl isomer **28**. The mixture was fractionated

by column chromatography (light petroleum–ethyl acetate, 4:1), to give **29** (15.2 g, 78.2%), m.p. 55–56° (from hexane), $[\alpha]_D$ −29° (*c* 0.7, chloroform), R_F 0.62, *T* 8.75 min [column (*b*)]; lit.[15] m.p. 55–56°, $[\alpha]_D$ −28.8° (*c* 1.28, chloroform). N.m.r. data: ^{1}H, δ 4.98 (s, 1 H, H-1), 3.40 (s, 3 H, OMe), 2.04 (s, 3 H, OAc), 1.62 (s, 3 H, CMe), 1.00 (d, 3 H, *Me*CH); ^{13}C, δ 109.9 (Me*C*Ph), 98.2 (C-1), 76.5 (C-2,3), 73.7 (C-4), 63.9 (C-5), 54.7 (OMe), 28.9 (*Me*CPh), 17.1 (C-6).

Methyl 4-O-acetyl-2,3-O-(S)-(1-phenylethylidene)-α-L-rhamnopyranoside (**28**). — A solution of **29** (4.8 g) in dichloromethane (20 mL) was isomerised by adding toluene-*p*-sulphonic acid (0.5 g), boiling under reflux for 4 h, and then storage for 12 h at 20°. Work-up, as described for **3**, gave a syrup (4.0 g, 83.3%) which contained 5% of the *endo*-phenyl isomer **29** and 95% of the *exo*-phenyl isomer **28** [g.l.c. column (*b*)]. Column chromatography (light petroleum–ethyl acetate, 4:1) of this mixture gave **28** (3.25 g, 67.7%), m.p. 72–73° (from hexane), $[\alpha]_D$ −59° (*c* 0.55, chloroform), R_F 0.70, *T* 9.52 min [column (*b*)]; lit.[15] m.p. 72–73°, $[\alpha]_D$ −59.1° (*c* 1.37, chloroform). N.m.r. data: ^{1}H, δ 4.90 (s, 1 H, H-1), 3.34 (s, 3 H, OMe), 2.12 (s, 3 H, OAc), 1.76 (s, 3 H, CMe), 1.20 (d, 3 H, *Me*CH); ^{13}C, δ 109.7 Me*C*Ph), 98.1 (C-1), 76.1 (C-2,3), 75.2 (C-4), 64.0 (C-5), 54.8 (OMe), 29.1 (*Me*CPh), 17.1 (C-6).

Methyl 2,3-O-(S)-(1-phenylethylidene)-α-L-rhamnopyranoside (**26**). — Compound **28** (1.7 g) was deacetylated as described for **1**, to give the *exo*-phenyl isomer **26** (1.46 g, 99%), m.p. 80–82° (from hexane), $[\alpha]_D$ −45° (*c* 0.8, chloroform), R_F 0.37 (light petroleum–ethyl acetate, 4:1). ^{1}H-N.m.r. data: δ 4.90 (s, 1 H, H-1), 3.28 (s, 3 H, OMe), 2.9 (bs, 1 H, OH), 1.68 (s, 3 H, OMe), 1.32 (d, 3 H, *Me*CH).

Anal. Calc. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.22; H, 7.16.

Methyl 2,3-O-(R)-(1-phenylethylidene)-α-L-rhamnopyranoside (**27**). — Compound **29** (5 g) was deacetylated as described for the preparation of **1**, to give the *endo*-phenyl isomer **27** (4.16 g, 96%), m.p. 68–69° (from hexane), $[\alpha]_D$ −35° (*c* 0.7, chloroform), R_F 0.37 (light petroleum–ethyl acetate, 4:1). ^{1}H-N.m.r. data: δ 4.97 (s, 1 H, H-1), 3.32 (s, 3 H, OMe), 2.24 (bs, 1 H, OH), 1.56 (s, 3 H, CMe), 1.10 (d, 3 H, CH_3CH).

Anal. Calc. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.30; H, 7.24.

Methyl 4-O-benzyl-2-O-methyl- (**31**) *and -3-O-methyl-α-L-rhamnopyranoside* (**32**). — Methyl 4-*O*-benzyl-2,3-*O*-methylene-α-L-rhamnopyranoside (**21**, 0.5 g) was treated with a refluxing solution of $LiAlH_4$ (0.2 g) and $AlCl_3$ (0.6 g) in ether–dichloromethane (20 mL, 1:1). After 80 h, t.l.c. (dichloromethane–acetone, 9:1) revealed [g.l.c., column (*c*)] three components in the ratios 70:24:6; R_F 0.82, 0.55, and 0.42. The crude product (0.470 g) was subjected to column chromatography (20 g). Elution with dichloromethane–acetone (9:1) gave, first, **21** (0.24 g).

Eluted second was **31** (0.07 g, 14%), $[\alpha]_D$ −64° (*c* 0.8, chloroform) (lit.[20] $[\alpha]_D$ −56°), R_F 0.55, *T* 1.43 min [column (*c*). ^{1}H-N.m.r. data: δ 7.40–7.16 (m, 5 H, Ph), 4.79 (q, 2 H, PhCH_2), 4.72 (s, 1 H, H-1), 3.86 (dd, 1 H, H-3), 3.70–3.10 (m, 3 H, H-2,4,5), 3.51 (s, 3 H, MeO-2), 3.34 (s, 3 H, MeO-1), 2.44 (d, 1 H, OH), 1.31 (d, 3 H, *Me*CH).

Anal. Calc. for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 64.10; H, 7.96.

Eluted third was **32** (0.021 g, 4%), $[\alpha]_D$ −81° (*c* 1.15, chloroform) {lit.[21] $[\alpha]_D$ −80° (*c* 1.1, chloroform)}, R_F 0.42, *T* 1.24 min [column (*c*)].

Anal. Found: C, 63.56; H, 8.00.

*Benzyl 4-O-ethyl-2-O-methyl-β-*L*-arabinopyranoside* (**30**). — A mixture of the *endo*-ethyl isomer **6** (0.4 g), dichloromethane (15 mL), ether (15 mL), $LiAlH_4$ (0.109 g), and $AlCl_3$ (0.380 g) was boiled under reflux for 1 h. Conventional work-up of the mixture gave a crude product (0.38 g, 94%), which was crystallised from cyclohexane (13 mL) to give **30** (0.21 g, 52.1%), m.p. 90–91°, $[\alpha]_D$ +230° (*c* 0.8, chloroform), R_F 0.38 (dichloromethane–ethyl acetate, 7:3), *T* 7.98 min [column (*f*)]. ^{1}H-N.m.r. data: δ 7.50–7.20 (m, 5 H, Ph), 5.04 (d, 1 H, H-1), 4.67 (q, 2 H, PhCH_2), 3.37 (s, 3 H, OMe), 2.67 (d, 1 H, OH), 1.22 (t, 3 H, *Me*CH_2); $J_{1,2}$ 3.5, $J_{2,3}$ 10.0, $J_{3,4}$ 4.0 Hz. After the addition of D_2O, the d at δ 2.67 disappeared and the m at δ 3.99 collapsed to a dd.

Anal. Calc. for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.85; H, 7.88.

*Hydrogenolysis of benzyl 3,4-O-(*R*)-ethylidene-2-O-methyl-β-*L*-arabinopyranoside* (**5**). — Compound **5** (0.04 g) was treated with $LiAlH_4$ (0.022 g) and $AlCl_3$ (0.038 g) in eher–dichloromethane (10 mL, 1:1) for 1 h at reflux temperature. The syrupy product (0.034 g, 84.4%) was a 31:69 mixture of **30** [*T* 7.98 min, column (*f*)] and, presumably, benzyl 3-*O*-ethyl-2-*O*-methyl-β-L-arabinopyranoside (*T* 7.32 min), but the mixture could not be fractionated.

Methyl 4-O-isopropyl- (**33**) *and 3-O-isopropyl-β-*L*-arabinopyranoside* (**37**). — A solution of **7**[9] (0.638 g) in ether–dichloromethane (20 mL, 1:1) was stirred with $LiAlH_4$ (0.356 g) and $AlCl_3$ (1.25 g) for 1.5 h at 20°. The usual work-up gave a syrup (0.6 g, 93%) containing 86% of **33** and 14% of **37** [g.l.c. of the acetates on column (*g*)]. The mixture was subjected to column chromatography (dichloromethane–acetone, 6:4). Eluted first was amorphous **37** (0.04 g, 6%), $[\alpha]_D$ +205° (*c* 0.2, chloroform), R_F 0.43, *T* 5.40 min [acetate on column (*g*)]. N.m.r. data: ^{1}H, δ 4.80 (d, 1 H, H-1), 3.70 (s, 3 H, OMe), 2.70 and 2.40 (2 bs, 2 H, HO-2,4), 1.25 and 1.18 (2 d, 6 H, CMe_2); ^{13}C, δ 100.02 (C-1), 76.76 (C-3), 71.25 (Me_2C), 61.85 (C-5), 55.49 (OMe), 23.29 and 22.39 (CMe_2).

Anal. Calc. for $C_9H_{18}O_5$: C, 52.41; H, 8.80. Found: C, 52.36; H, 8.77.

Eluted second was amorphous **33** (0.38 g, 59%), $[\alpha]_D$ +216° (*c* 0.5, chloroform), R_F 0.38 (dichloromethane–acetone, 6:4), *T* 5.72 min [acetate on column (*g*)]. N.m.r. data: ^{1}H, δ 4.80 (d, 1 H, H-1), 3.45 (s, 3 H, OMe), 2.35 and 2.12 (2 bs, 2 H, HO-2,3), 1.23 and 1.18 (2 d, 6 H, CMe_2); ^{13}C, δ 99.83 (C-1), 73.98 (C-4), 70.92 (CMe_2), 60.64 (C-5), 55.55 (OMe), 23.05 and 21.99 (CMe_2).

Anal. Found: C, 52.45; H, 8.84.

*Benzyl 4-O-isopropyl-β-*L*-arabinopyranoside* (**34**). — Benzyl 3,4-*O*-isopropylidene-β-L-arabinopyranoside[10] (**8**, 0.75 g) was hydrogenolysed with $LiAlH_4$ (0.204 g) and $AlCl_3$ (0.71 g) in ether–dichloromethane (40 mL, 1:1) for 8 h at reflux temperature. The syrupy, crude product (0.648 g), obtained after the usual work-up, contained two components in the ratio 82:18 [g.l.c. column (*i*) after acetyla-

tion]. The main product crystallised from ether, to give **34** (0.5 g, 66%), m.p. 61–63°, $[\alpha]_D$ +181° (*c* 0.7, chloroform), *T* 10.27 min [acetate on column (*i*)]. When **34** (0.05 g) was treated with $NaIO_4$ (0.062 g) in ethanol–water (3 mL, 1:1) for 10 min, complete reaction occurred (t.l.c.).

Anal. Calc. for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 64.00; H, 7.77.

Benzyl 2-O-benzyl-4-O-isopropyl-β-L-arabinopyranoside (**35**). — Compound **9** (0.240 g) was treated with $LiAlH_4$ (0.047 g) and $AlCl_3$ (0.172 g) in ether–dichloromethane (20 mL, 1:1) for 10 min at reflux temperature. The usual work-up gave a crystalline residue (0.221 g, 91.6%) which contained two components in the ratio 95:5 (g.l.c.). Recrystallisation of the mixture from cyclohexane gave **35** (0.102 g, 42.3%), m.p. 73–74°, $[\alpha]_D$ +177° (*c* 0.6, chloroform), R_F 0.32 (light petroleum–ethyl acetate, 7:3), *T* 5.52 min [column (*d*)]. ^{1}H-N.m.r. data: δ 7.40–7.10 (m, 10 H, 2 Ph), 4.89 (d, 1 H, H-1), 4.61 and 4.59 (2 q, 4 H, 2 PhC*H*$_2$), 4.04 (m, 1 H, H-3), 3.87–3.55 (m, 5 H, H-2,4,5,5′ and C*H*Me$_2$), 2.42 (d, 1 H, OH), 1.20 and 1.14 (2 d, 6 H, CMe$_2$); $J_{1,2}$ 3.5, $J_{2,3}$ 10.0, $J_{3,4}$ 3.6, $J_{H,OH}$ 7, $J_{CH,Me}$ 1.6 Hz.

The minor component, R_F 0.23 and *T* 4.74 min, was not isolated.

Benzyl 4-O-isopropyl-2-O-methyl-β-L-arabinopyranoside (**36**). — Compound **10** (1.50 g) was treated with $LiAlH_4$ (0.39 g) and $AlCl_3$ (1.36 g) in ether–dichloromethane (40 mL, 1:1) for 15 min at reflux temperaure. G.l.c. showed that the syrup (1.35 g, 89%), obtained after the usual work-up, contained **36** (97%) and, presumably, benzyl 3-*O*-isopropyl-2-*O*-methyl-β-L-arabinopyranoside (3%). The impurity was removed by column chromatography (Kieselgel G, 100 g), using dichloromethane–acetone (9:1), to give **36** (1.10 g, 73%), $[\alpha]_D$ +206° (*c* 0.9, chloroform), R_F 0.68 (dichloromethane–acetone, 9:1). ^{1}H-N.m.r. data: δ 7.50–7.25 (m, 5 H, Ph), 5.03 (d, 1 H, H-1), 4.67 (q, 2 H, PhC*H*$_2$), 3.98 (m, 1 H, H-3), 3.82–3.63 (m, 4 H, H-4,5,5′ and C*H*Me$_2$), 3.46 (dd, 1 H, H-2), 3.41 (s, 3 H, OMe), 2.43 (d, 1 H, OH), 1.24 and 1.17 (2 s, 6 H, CMe$_2$); $J_{1,2}$ 3.6, $J_{2,3}$ 9.6 Hz. After addition of D_2O, the d at δ 2.43 disappeared and the m at δ 3.98 collapsed to a dd.

Anal. Calc. for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16. Found: C, 65.02; H, 8.10.

Methyl 2-O-isopropyl-α-L-rhamnopyranoside (**38**). — A solution of **22**[11] (0.700 g) in ether–dichloromethane (20 mL, 1:1) was stirred with $LiAlH_4$ (0.364 g) and $AlCl_3$ (1.280 g) for 20 min at 20°. The usual work-up gave a syrup (0.450 g, 64%) containing 96% of **38** [g.l.c. of the acetate on column (*g*)]. This compound was purified by column chromatography (dichloromethane–acetone, 6:4), to give syrupy **38** (0.420 g, 60%), $[\alpha]_D$ −14° (*c* 0.8, chloroform), R_F 0.60, *T* 5.36 min [acetate on column (*g*)]. N.m.r. data: ^{1}H, δ 4.65 (s, 1 H, H-1), 3.37 (s, 3 H, OMe), 2.82 and 2.50 (2 bs, 2 H, HO-3,4), 1.32 (d, 3 H, H-6,6,6), 1.18 and 1.20 (2 d, 6 H, CMe$_2$); ^{13}C, δ 99.27 (C-1), 76.24 (C-2), 74.05 (C-4), 72.28 (C-3), 67.41 (C-5), 71.30 (*C*HMe$_2$), 54.64 (OMe), 23.11 and 22.00 (C*Me*$_2$), 17.53 (C-6).

Anal. Calc. for $C_{10}H_{20}O_5$: C, 54.53; H, 9.15. Found: C, 54.49; H, 9.20.

Methyl 4-O-benzyl-2-O-isopropyl- (**39**) *and -3-O-isopropyl-α-L-rhamnopyranoside* (**43**). — Methyl 4-*O*-benzyl-2,3-*O*-isopropylidene-α-L-rhamnopyranoside[12] (**23**, 1.40 g) was hydrogenolysed with $LiAlH_4$ (0.259 g) and $AlCl_3$

(0.908 g) in ether–dichloromethane (50 mL, 1:1) for 80 min at room temperature. The usual work-up gave a crude syrup (1.33 g, 95%) which contained two components in the ratio 83:17. Column chromatography on Kieselgel G (80 g), using chloroform–acetone (95:5), gave, first, **39** (0.75 g, 53.5%), $[\alpha]_D$ −30° (*c* 2, chloroform). ^{13}C-N.m.r. data: δ 97.6 (C-1), 76.6 (C-2), 72.1 (C-3), 82.1 (C-4), 67.0 (C-5), 17.9 (C-6), 55.1 (OMe), 71.1 (*C*HMe$_2$), 75.0 (*C*H$_2$Ph), 23.0 and 22.1 (C*Me*$_2$).

Anal. Calc. for $C_{17}H_{26}O_5$: C, 65.78; H, 8.44. Found: C, 66.03; H, 8.40.

Eluted second was **43** (0.19 g, 13.5%), $[\alpha]_D$ −69° (*c* 1.2, chloroform), R_F 0.26. ^{13}C-N.m.r. data: δ 97.5 (C-1), 69.6 (C-2), 77.5 (C-3), 80.0 (C-4), 67.4 (C-5), 17.9 (C-6), 55.0 (OMe), 71.2 (*C*HMe$_2$), 75.2 (*C*H$_2$Ph), 23.4 and 22.5 (CH*Me*$_2$).

Anal. Calc. for $C_{17}H_{26}O_5$: C, 65.78; H, 8.44. Found: C, 66.08; H, 8.29.

*Benzyl 2-O-isopropyl-α-*L*-rhamnopyranoside* (**40**). — Benzyl 2,3-O-*isopropylidene-α-*L*-rhamnopyranoside[13] (**24**, 1.47 g) was treated with $LiAlH_4$ (0.285 g) and $AlCl_3$ (1 g) in ether–dichloromethane (40 mL, 1:1) for 2 h at reflux temperature. The usual work-up gave a crude syrup (1.30 g, 87.8%) which was 99.1% pure [g.l.c. of the acetate on column (*g*)]; $[\alpha]_D$ −54° (*c* 0.8, chloroform), R_F 0.64 (dichloromethane–methanol, 97:3). ^{13}C-N.m.r. data: δ 97.52 (C-1), 76.29 (C-2), 72.26 (C-3), 73.77 (C-4), 67.87 (C-5), 17.50 (C-6), 71.23 (*C*HMe$_2$), 68.5 (PhCH$_2$), 22.89 and 21.93 (CH*Me*$_2$). A solution of the syrup (0.135 g) in ethanol–water (6 mL, 1:1) containing $NaIO_4$ (0.195 g) underwent complete reaction in 5 min, confirming the position of the isopropyl group.

Anal. Calc. for $C_{16}H_{24}O_5$: C, 68.84; H, 8.15. Found: C, 69.05; H, 8.10.

*Benzyl 3,4-di-O-acetyl-2-O-isopropyl-α-*L*-rhamnopyranoside* (**41**). — Compound **40** (0.345 g) was acetylated with pyridine (3 mL) and acetic anhydride (3 mL) for 48 h at room temperature. Conventional work-up gave syrupy **41** (0.37 g, 83%), $[\alpha]_D$ −58° (*c* 0.5, chloroform), *T* 12.48 min [column (*j*)]. ^{13}C-N.m.r. data: δ 98.27 (C-1), 74.33 (C-2), 71.47 (C-3), 73.02 (C-4), 66.47 (C-5), 17.37 (C-6), 71.26 (*C*HMe$_2$), 68.90 (PhCH$_2$), 22.89 and 21.93 (CH*Me*$_2$).

Anal. Calc. for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 63.65; H, 7.51.

Benzyl 4-O-benzyl-2-O-isopropyl- (**42**) *and -3-O-isopropyl-α-*L*-rhamnopyranoside* (**44**). — Compound **25**[14] (0.9 g) was cleaved with $LiAlH_4$ (0.134 g) and $AlCl_3$ (0.467 g) in ether–dichloromethane (20 mL, 1:1) at reflux temperature. After 20 min, **25** had disappeared and two components in the ratio 68:32 were detected by t.l.c. (dichloromethane–acetone, 9:1) or by g.l.c. The crude syrup (0.84 g), obtained after the usual work-up, was subjected to column chromatography (dichloromethane–acetone, 9:1). Eluted first was **42** (0.54 g, 60%), $[\alpha]_D$ −50° (*c* 1, chloroform), R_F 0.66, *T* 13.12 min [acetate on column (*k*)]. ^{13}C-N.m.r. data: δ 97.43 (C-1), 76.87 (C-2), 72.38 (C-3), 82.31 (C-4), 67.15 (C-5), 17.94 (C-6), 68.87 (PhCH$_2$-1), 74.93 (PhCH$_2$-4), 71.32 (Me$_2$CH), 22.03 and 22.97 (CH*Me*$_2$).

Anal. Calc. for $C_{23}H_{30}O_5$: C, 71.47; H, 7.82. Found: C, 72.01; H, 7.68.

Eluted second was syrupy **44** (0.14 g, 15%), $[\alpha]_D$ −71° (*c* 0.3, chloroform), R_F 0.45, *T* 12.55 min [acetate on column (*k*)]. ^{13}C-N.m.r. data: δ 98.37 (C-1), 69.84

(C-2), 77.72 (C-3), 80.00 (C-4), 67.63 (C-5), 17.92 (C-6), 69.11 (PhCH$_2$-1), 75.42 (PhCH$_2$-4), 71.30 (Me$_2$CH), 22.51 and 23.53 (CH*Me*$_2$).

Anal. Found: C, 71.90; H, 7.89.

Methyl 4-O-(RS)-(1-phenylethyl)-β-L-arabinopyranoside (**45**). — A solution of **12** (0.364 g) in ether–dichloromethane (20 mL, 1:1) was stirred with $LiAlH_4$ (0.16 g) and $AlCl_3$ (0.56 g) for 30 min at 20°. The usual work-up gave a syrup (0.325 g, 89%) containing 82% of **45** [g.l.c. on column (*l*)]. This compound was purified by column chromatography (dichloromethane–acetone, 6:4), to give **45** (0.25 g, 68%), $[\alpha]_D$ +178° (*c* 0.4, chloroform), R_F 0.53, *T* 6.32 and 6.58. ^{1}H-N.m.r. data: δ 4.80 (d, 1 H, H-1), 4.68 (q, 1 H, MeC*H*Ph), 3.40 (s, 3 H, OMe), 2.20–2.55 (m, 2 H, HO-2,3).

Anal. Calc. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.70; H, 7.55.

Benzyl 2-O-benzyl-4-O-(R)- (**46**) *and -(S)-(1-phenylethyl)-β-L-arabinopyranoside* (**47**). — Compound **20** (1.0 g) was treated with $LiAlH_4$ (0.167 g) and $AlCl_3$ (0.615 g) in ether–dichloromethane (30 mL, 1:1) for 10 min at reflux temperature. The usual work-up gave a syrupy product (0.973 g) containing two components in a ratio of 1:1 (t.l.c.), which were isolated by chromatography on a column of Kieselgel G (80 g), using light petroleum–ethyl acetate (7:3). Eluted first was **46** (0.31 g, 31%), m.p. 109° (from cyclohexane), $[\alpha]_D$ +176° (*c* 1.3, chloroform), R_F 0.44. ^{1}H-N.m.r. data: δ 7.40–7.10 (m, 15 H, 3 Ph), 4.91 (d, 1 H, H-1), 4.77–4.39 (m, 5 H, 2 PhC*H*$_2$ and PhC*H*Me), 3.95 (m, 1 H, H-3), 3.73 (dd, 1 H, H-2), 3.75–3.53 (m, 3 H, H-4,5,5′), 2.36 (d, 1 H, OH), 1.47 (d, 3 H, PhCH*Me*); $J_{1,2}$ 3.3, $J_{2,3}$ 9.6, $J_{3,4}$ 3.6, $J_{H,OH}$ 7, $J_{CH,Me}$ 6.6 Hz. After the addition of D_2O, the d at δ 2.36 disappeared and the m at δ 3.95 collapsed to a dd.

Anal. Calc. for $C_{27}H_{30}O_5$: C, 74.63; H, 6.96. Found: C, 74.50; H, 7.00.

Eluted second was **47** (0.295 g, 29.5%), m.p. 95–97° (from cyclohexane), $[\alpha]_D$ +107° (*c* 0.55, chloroform), R_F 0.38. ^{1}H-N.m.r. data: δ 7.40–7.10 (m, 15 H, 3 Ph), 4.93 (d, 1 H, H-1), 4.82–4.35 (m, 5 H, 2 PhC*H*$_2$ and PhC*H*Me), 4.08 (m, 1 H, H-3), 3.80 (dd, 1 H, H-2), 3.74–3.65 (m, 1 H, H-4), 3.60 and 3.35 (2 dd, 2 H, H-5,5′), 2.64 (d, 1 H, OH), 1.46 (d, 3 H, PhCH*Me*); $J_{1,2}$ 3.2, $J_{2,3}$ 9.6, $J_{3,4}$ 3.6, $J_{4,5}$ 1.8, $J_{4,5'}$ 2.8, $J_{5,5'}$ 12.2, $J_{H,OH}$ 6, $J_{CH,Me}$ 6.4 Hz. After addition of D_2O, the d at δ 2.64 disappeared and the m at δ 4.08 collapsed to a dd.

Anal. Calc. for $C_{27}H_{30}O_5$: C, 74.63; H, 6.96. Found: C, 74.80; H, 7.05.

Methyl 2-O-(R)- (**48**) *and -(S)-(1-phenylethyl)-α-L-rhamnopyranoside* (**49**). — A solution of **27** (1.01 g) in ether–dichloromethane (20 mL, 1:1) was treated with $LiAlH_4$ (0.417 g) and $AlCl_3$ (1.466 g) for 30 min at 20°. The usual work-up gave a syrup (0.940 g, 92%) containing two components in the ratio 1:1 [g.l.c. of the acetate form, column (*e*)]. The compounds were isolated by column chromatography (light petroleum–ethyl acetate, 4:6). Eluted first was **48** (0.35 g, 34%), m.p. 96–98° (from ethyl acetate–hexane, $[\alpha]_D$ +70° (*c* 1, chloroform), R_F 0.53, *T* 8.43 min [acetate on column (*e*)]. N.m.r. data: ^{1}H, δ 4.76 (s, 1 H, H-1), 4.57 (q, 1 H, MeC*H*Ph), 3.33 (s, 3 H, OMe), 1.47 (d, 3 H, *Me*CHPh), 1.31 (d, 3 H, H-6,6,6); ^{13}C, δ 98.32 (C-1), 77.58 (MeCHPh), 75.77 (C-2), 73.91 (C-4), 71.24 (C-3), 67.58 (C-5), 54.70 (OMe), 23.94 (*Me*CHPh), 17.59 (C-6).

Anal. Calc. for $C_{15}H_{22}O_5$: C, 63.81; H, 7.86. Found: C, 63.84; H, 7.88.

Eluted second was **49** (0.28 g, 28%), m.p. 104° (from ethyl acetate–hexane), $[\alpha]_D$ −61° (*c* 0.7, chloroform), R_F 0.43, *T* 7.90 min [acetate on column (*e*)]. N.m.r. data: ^{1}H, δ 4.65 (q, 1 H, MeC*H*Ph), 4.29 (s, 1 H, H-1), 3.16 (s, 3 H, OMe), 1.50 (d, 3 H, *Me*CHPh), 1.33 (d, 3 H, H-6,6,6); ^{13}C, δ 99.25 (C-1), 79.43 (Me*C*HPh), 77.48 (C-2), 74.03 (C-4), 71.73 (C-3), 67.52 (C-5), 54.52 (OMe), 23.30 (*Me*CHPh), 17.56 (C-6).

Anal. Calc. for $C_{15}H_{22}O_5$: C, 63.81; H, 7.86. Found: C, 63.79; H, 7.82.

*Hydrogenolysis of methyl 2,3-O-(S)-(1-phenylethylidene)-α-*L*-rhamnopyranoside* (**26**). — To a solution of **26** (0.196 g) in ether–dichloromethane (8 mL, 1:1) were added $LiAlH_4$ (0.08 g) and $AlCl_3$ (0.279 g). After the mixture had been boiled under reflux for 8 h, t.l.c. (light petroleum–ethyl acetate, 4:6) revealed two products in the ratio 58:42, which were identical with **48** and **49** [g.l.c. of the acetates on column (*e*)]. Physical and spectroscopic data corresponded to those of the compounds obtained by the hydrogenolysis of **27**.

REFERENCES

1 S. S. Bhattacharjee and P. A. J. Gorin, *Can. J. Chem.*, 47 (1969) 1195–1206.
2 S. S. Bhattacharjee and P. A. J. Gorin, *Can. J. Chem.*, 47 (1969) 1207–1215.
3 A. Lipták, *Tetrahedron Lett.*, (1976) 3551–3554.
4 A. Lipták, P. Fugedi, and P. Nánási, *Carbohydr. Res.*, 51 (1976) c19–c21.
5 A. Lipták, V. A. Oláh, and J. Kerékgyártó, *Synthesis*, (1982) 421–423.
6 M. A. Oldham and J. Honeyman, *J. Chem. Soc.*, (1946) 986–989.
7 J. G. Buchanan and A. R. Edgar, *Carbohydr. Res.*, 49 (1976) 289–304.
8 P. J. Garegg, K. B. Lindberg, and C. G. Swahn, *Acta Chem. Scand., Ser. B*, 28 (1974) 381–384.
9 J. Honeyman, *J. Chem. Soc.*, (1946) 990–993.
10 C. E. Ballou, *J. Am. Chem. Soc.*, 79 (1957) 165–166.
11 P. A. Levene and I. E. Muskat, *J. Biol. Chem.*, 105 (1934) 431–442.
12 A. H. Haines, *Carbohydr. Res.*, 10 (1969) 466–467.
13 J. S. Brimacombe and L. C. N. Tucker, *Carbohydr. Res.*, 5 (1967) 36–44.
14 A. H. Haines, *Carbohydr. Res.*, 1 (1965) 214–228.
15 H. Lotter and A. Lipták, *Z. Naturforsch., Teil B*, 36 (1981) 997–999.
16 D. M. Clode, *Chem. Rev.*, 79 (1979) 491–513.
17 B. H. Lipshutz and M. C. Morey, *J. Org. Chem.*, 46 (1981) 2419–2423.
18 J. Harangi, A. Lipták, V. A. Oláh, and P. Nánási, *Carbohydr. Res.*, 98 (1981) 165–171.
19 A. Lipták, *Carbohydr. Res.*, 63 (1978) 69–75.
20 V. Pozsgai, *Carbohydr. Res.*, 69 (1979) 284–286.
21 V. Pozsgai and P. Nánási, *Carbohydr. Res.*, 81 (1980) 184–186.
22 Z. Szurmai, A. Lipták, J. Harangi, and P. Nánási, *Acta Chim. Acad. Sci. Hung.*, 107 (1981) 213–219.
23 A. Lipták, P. Nánási, A. Neszmélyi, and H. Wagner, *Tetrahedron*, 36 (1980) 1261–1268.
24 P. Fugedi, A. Lipták, P. Nánási, and J. Szejtli, *Carbohydr. Res.*, 104 (1982) 55–67.
25 A. Lipták and P. Fugedi, *Angew. Chem.*, 95 (1983) 245–246.
26 J. E. McCormick, *Carbohydr. Res.*, 4 (1967) 262–263.
27 D. M. Clode, D. Horton, and W. Weckerle, *Carbohydr. Res.*, 49 (1976) 305–314.
28 R. Kuhn, H. Trischmann, and I. Löw, *Angew. Chem.*, 67 (1955) 32.