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SYNTHESIS AND DIAZOMETHANE-CATALYSED 1→2 ACYL MIGRATION OF THE L-ARABINOSYL ESTERS OF *N*-ACYLAMINO ACIDS

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ABSTRACT

The fully benzylated α- and β-L-arabino-pyranosyl (**1** and **2**) and -furanosyl esters (**3** and **4**) of *N*-acetyl-D-alanine and *N*-*tert*-butoxycarbonyl-L-phenylalanine have been synthesised. Catalytic hydrogenation of **3** and **4** gave both anomers of 1-*O*-(*N*-*tert*-butoxycarbonyl-L-phenylalanyl)-L-arabino-pyranose (**5**) and -furanose (**6**), which were characterised as the triacetates **7** and **8**, respectively. Treatment of the *cis*-oriented β-anomers of **5** and **6** with 0.5 equiv. of diazomethane at 0° for 1 h led to the 1→2 acyl rearrangement, with pyranose–furanose interconversion and anomerisation, to give, upon acetylation, a mixture of 1,3,4- and 1,3,5-tri-*O*-acetyl-2-*O*-(*N*-*tert*-butoxycarbonyl-L-phenylalanyl)-α,β-L-arabino-pyranose and -furanose, the structures of which were determined by ^{1}H- and ^{13}C-n.m.r. spectroscopy. The 1→2 acyl-migration step in the L-*arabino* series is immediately followed by isomerisation into the four possible forms.

INTRODUCTION

We have shown that diazomethane catalyses the 1→2 rearrangement of 1-*O*-(*N*-acylaminoacyl)-α-D-glucopyranose[1–3] and -glucopyranuronates[4] with high retention of anomeric configuration. The reaction was explained in terms of a base-catalysed interchange in which diazomethane functions as a base towards HO-2. We now report on reactions in the L-arabinose series.

Tejima and Fletcher[5] found that, in aqueous pyridine, the α-furanose and α-pyranose forms of 1-*O*-benzoyl-L-arabinose were stable, whereas each of the corresponding β-forms readily underwent 1→2 acyl rearrangement to yield 2-*O*-benzoyl-L-arabinopyranose. Also, although the rate of mutarotation of 1-*O*-benzoyl-β-L-arabinofuranose was much higher than that of the corresponding pyranose form, it was significantly lower than that of 2-*O*-benzoyl-β-L-arabinopyranose.

In the D-*gluco* series, glycosyl esters of *N*-*tert*-butoxycarbonyl-L-phenylalanine showed considerable resistance toward hydrolysis of the C-1 ester bond, and, therefore, this *N*-acylamino acid was used in the present study.

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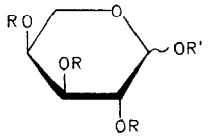
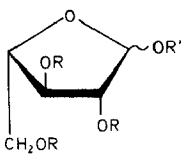
RESULTS AND DISCUSSION

The protected L-arabino-pyranosyl and -furanosyl esters **1** (45%) and **2** (50%) were obtained as α,β-mixtures by the imidazole-promoted dicyclohexylcarbodiimide condensation[6] of *N*-acetyl-D-alanine with 2,3,4-tri-*O*-benzyl-β-L-arabinopyranose[5,7] and 2,3,5-tri-*O*-benzyl-β-L-arabinofuranose[5,7], respectively. The synthesis of the analogous 1-esters **3** (65%) and **4** (80%), from *N-tert*-butoxycarbonyl-L-phenylalanine, was effected by the accelerated active-ester method[6] by reaction for 2 h in the presence of a large excess (10 equiv.) of imidazole. The anomers of **1–4** were isolated and characterised; in each series, the 1,2-*trans* α-anomer markedly preponderated and extensive column chromatography was required to isolate the corresponding 1,2-*cis* β-anomer.





1 R=Bzl , R'=Ac–D–Ala– **2** R=Bzl , R'=Ac–D–Ala–

3 R=Bzl , R'= X **4** R=Bzl , R'= X

5 R=H , R'= X **6** R=H , R'= X

7 R=Ac , R'= X **8** R=Ac , R'= X

X = *N*-*tert*-butoxycarbonyl-L-phenylalanyl

Catalytic hydrogenation of the α and β anomers of **1** and **2** in 2-methoxyethanol–acetic acid proceeded with concomitant hydrolysis of the C-1 ester bond. The latter reaction could be markedly suppressed by using dry ethyl acetate as the solvent, but the insoluble products were deposited on the catalyst surface and decomposed during the extraction. Analogous deprotection of the α and β anomers of **3** and **4** led to the 1-esters **5**α, **5**β, **6**α, and **6**β. The 1,2-*trans* L-arabinopyranosyl ester **5**α was crystalline, but the other compounds were obtained as hygroscopic syrups contaminated with 10–20% of L-arabinose. The triacetates **7**α, **7**β, **8**α, and **8**β were isolated pure and characterised.

The structures of the above triacetates were deduced from their ^{1}H-n.m.r. spectra (Table I). The signals for H-1 of **7**α and **7**β were doublets with $J_{1,2}$ values (6.2 and 2.8 Hz, respectively) consistent with the 2,3,4-tri-*O*-acetyl-1-*O*-(*N-tert*-butoxycarbonyl-L-phenylalanyl)-α- and -β-L-arabinopyranose structure (*i.e.*, 1,2-*trans* and 1,2-*cis*, respectively). The structure of **7**α was confirmed by independent synthesis involving the condensation of 2,3,4-tri-*O*-acetyl-L-arabinopyranose[8] with *N-tert*-butoxycarbonyl-L-phenylalanine pentachlorophenyl ester and resolution of the resulting α,β-mixture. The structures of 2,3,5-tri-*O*-acetyl-1-*O*-(*N-tert*-butoxycarbonyl-L-phenylalanyl)-α- (**8**α) and -β-L-arabinofuranose (**8**β) were in-

TABLE I

N.M.R. DATA FOR **7–8** AND THE ISOMERIC MIXTURES **9**[a]

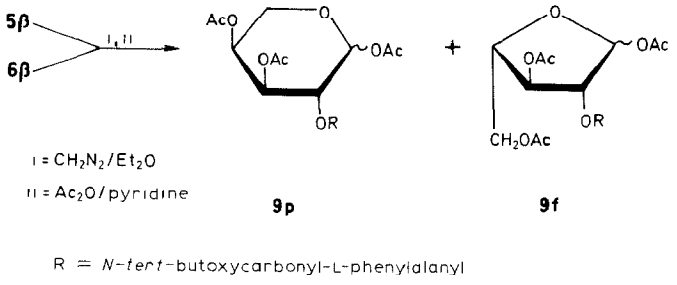
Compound	*^{1}H-N.m.r. data*				*^{13}C-N.m.r. data*
	H-1 (δ)	*$J_{1,2}$ (Hz)*	*AcO (δ)*	*^{t}Bu (δ)*	*C-1 (δ)*
7α	5.76 d	6.26	2.13, 2.08, 2.05	1.40	92.38
7β	6.37 d	2.8	2.15, 2.02, 2.00	1.40	
8α	6.41 s		2.12 (2), 2.10	1.42	99.77
8β	6.42 d	3.5	2.10, 2.08, 2.06	1.40	
9[bc]	6.41 d	2.8	2.17, 2.15, 2.14,	1.40	99.04
	6.19 s		2.13, 2.12, 2.10,	1.39	92.10
	5.68 d	7.0	2.08, 2.00, 1.99	1.38	89.89
9[bd]	6.41 d	2.8	2.18, 2.16, 2.15,	1.41	
	6.19 s		2.13, 2.12, 2.11,	1.40	
	5.68 d	7.0	2.09, 2.01, 2.00	1.38	
9[be]	6.41 d	2.8	2.17, 2.15, 2.14,	1.41	99.47
	6.22 d	2.0	2.12, 2.11, 2.10,	1.40	95.38
	6.14 s		2.08, 2.00, 1.99	1.38	92.31
	5.68 d	7.0			89.96

[a]For solutions in $CDCl_3$. [b]The acetylated product from the reaction of: [c]**5β** and CH_2N_2 in *N,N*-dimethylformamide; [d]**6β** in *N,N*-dimethylformamide; [e]**6β** and CH_2N_2 in EtOAc.

dicated by the signals (s and d, *J* 3.5 Hz) for H-1 and by the $[\alpha]_D$ values (−25° and +40°, respectively). The finding that the L-arabinofuranosyl forms were more levorotatory than the corresponding L-arabinopyranosyl forms of the same anomeric configuration accords with the generalisation made by Tejima and Fletcher[5] for the L-*arabino* series. Thus, the formation of **5** and **6**, by catalytic hydrogenolysis of **3** and **4**, proceeded with retention of the ring size and anomeric configuration.

The 1→2 acyl migration of the L-arabino-pyranosyl (**5**) and -furanosyl esters (**6**) in *N,N*-dimethylformamide or dry ethyl acetate effected with various amounts of diazomethane at 0° for 1 h was studied. The resulting mixtures were acetylated, and the products were isolated by chromatography, and analysed by ^{1}H- and ^{13}C-n.m.r. spectroscopy. As expected, the 1,2-*trans* compounds **5α** and **6α** were not affected by diazomethane (0.5–5 equiv.), but the 1,2-*cis* compound **5β**, in either *N,N*-dimethylformamide or dry ethyl acetate with 0.5 equiv. of diazomethane, underwent 1→2 acyl rearrangement and pyranose–furanose interconversion to give, after acetylation, a mixture identified, on the basis of ^{1}H- and ^{13}C-n.m.r. data (see below and Table I), as containing 1,3,4-tri-*O*-acetyl-2-*O*-(*N*-*tert*-butoxycarbonyl-L-phenylalanyl)-L-arabinopyranose (**9***p*) and 1,3,5-tri-*O*-acetyl-2-*O*-(*N*-*tert*-butoxycarbonyl-L-phenylalanyl)-L-arabinofuranose (**9***f*). In *N,N*-dimethylformamide in the absence of diazomethane, **5β** was stable; under similar conditions, the L-arabinofuranosyl ester **6β** underwent 1→2 acyl rearrangement to give, after acetylation, a mixture of products **9***p*–**9***f*. In dry ethyl acetate, **6β** was stable.

The components of the mixture **9** could not be separated by t.l.c. or column



chromatography, but microanalytical data indicated that no decomposition products were present. The structures of the components were established by a comparison of the n.m.r. data with those of the related 1-esters **7** and **8**, and with literature data[9–12]; integration of the signals for anomeric protons gave the proportions of the isomeric forms present[13]. The ^{1}H-n.m.r. spectra of the mixtures always contained (Table I) three signals for anomeric protons (δ 5.58, 6.46, and 6.19) which were assigned to the α-pyranose, β-pyranose, and α-furanose components, respectively. The spectrum of the product mixture formed by treatment of **6β** in ethyl acetate with diazomethane contained an additional signal (δ 6.22) which was assigned to the β-furanose component. A comparison of the chemical shifts of the acetoxy signals (total intensity, nine protons) of the mixture **9** with those observed for the triacetates **7** and **8** revealed: (*a*) a low-field signal that was absent from the spectra of **7** and **8**, and (*b*) the absence of one of the signals associated with **7α** (δ 2.05) and one with **7β** (δ 2.02), respectively. The *tert*-butoxycarbonyl protecting-group gave three narrow-spaced singlets that integrated for nine protons; the chemical shifts of such resonances are affected[4] by the position of the *tert*-butoxycarbonylaminoacyl residue in the sugar ring and by the anomeric configuration. In

TABLE II

COMPOSITIONS OF THE ACETYLATED 2-*O*-(*N*-*tert*-BUTOXYCARBONYL-L-PHENYLALANYL)-L-ARABINOSE ISOMERS IN **9** AS DETERMINED BY N M R SPECTROSCOPY

Reaction conditions[a]		*Nucleus*	*Composition (%)*			
Starting compound	*Solvent*		*Pyranose*		*Furanose*	
			α	β	α	β
5β	$HCONMe_2$	^{1}H	60	30	10	n.d.[b]
5β	EtOAc	^{1}H	40	48	12	n d.
		^{13}C	35	50	10	n.d.
6β[c]	$HCONMe_2$	^{1}H	60	30	10	n.d.
		^{13}C	60	30	10	n d
6β	EtOAc	^{1}H	35	45	13	6

[a] 0.5 Equiv of diazomethane, 0°, 1 h. [b] Not detectable (<5%). [c] No diazomethane added.

the ^{13}C-n.m.r. spectra of the mixture **9**, the readily distinguished signals for anomeric carbons (δ 92.1, 89.9, and 99.0) were assigned to the α-pyranose, β-pyranose, and α-furanose components, respectively. In the spectrum of **9**, originating from diazomethane-treated **6β**, a fourth C-1 signal (δ 95.3) was clearly detectable and was assigned to the β-furanose form.

As can be seen from Table II, the pyranose forms preponderated in mixtures **9**, but the α,β-ratio varied with the solvent used in the migration step. The proportion of the α-furanose component was almost constant, even in the mixtures containing the β-furanose component.

In contrast to the D-*gluco* series[2,3], the 1→2 acyl rearrangement in the L-*arabino* series is followed immediately by isomerisation into the four possible forms. Liptak *et al.*[12], using ^{13}C-n.m.r. spectroscopy, showed that, in di- and oligosaccharides having L-arabinose at the reducing end, the latter exists as α and β pyranose and furanose forms.

EXPERIMENTAL

General methods. — Melting points were determined in capillaries and are uncorrected. Optical rotations were determined for 1% solutions in chloroform, unless otherwise stated. Concentrations were performed at <45° under diminished pressure using a rotary evaporator. Organic solutions were dried with anhydrous sodium sulphate. Column chromatography was performed on Silica Gel (Merck, 0.05–0.2 mm) and t.l.c. on Kieselgel G60 (Merck), using *A*, benzene–ethyl acetate (various proportions); *B*, ether–light petroleum (various proportions); *C*, chloroform–methanol (7:1); *D*, ethyl acetate–hexane (1:1); and detection with ninhydrin or by charring with sulphuric acid. N.m.r. spectra (internal Me_4Si) were recorded with a JEOL JNM FX-100 spectrometer (100 MHz for ^{1}H, 25 MHz for ^{13}C) for solutions in $CDCl_3$ if not stated otherwise. Signal intensities (C-1) in ^{13}C-n.m.r. spectra were obtained with inverse gated-proton-decoupling. The amount of diazomethane in ethereal solutions (redistilled before use) was determined by titration of an aliquot with benzoic acid, and the concentration of the reagent was adjusted to ~0.5 mmol/mL.

1-O-(N-Acetyl-D-alanyl)-2,3,4-tri-O-benzyl-L-arabinopyranose (**1**). — To a solution of 2,3,4-tri-*O*-benzyl-β-L-arabinopyranose[5,7] (1.26 g, 3 mmol), *N*-acetyl-D-alanine (400 mg, 3 mmol), and imidazole (420 mg, 6 mmol) in dichloromethane (16 mL) was added a solution of dicyclohexylcarbodiimide (620 mg, 3 mmol) in dichloromethane (2 mL) at 0° and the mixture was stirred at room temperature for 24 h. *N,N'*-Dicyclohexylurea was removed, and the filtrate was washed with water, M HCl, water, saturated aqueous sodium hydrogencarbonate, and water, dried, and concentrated. The residue was subjected to column chromatography (solvent *A*, 2:1), and the fractions containing the faster-moving **1α** were combined and concentrated. Crystallisation of the residue from isopropyl ether afforded **1α** (650 mg, 41%), m.p. 143–146°, $[\alpha]_D$ +13°. N.m.r. data: ^{1}H, δ 7.26 (Ph), 5.70 (d, $J_{1,2}$ 5.1 Hz, H-1), 1.94 (s, Ac*N*), 1.34 (d, *J* 7 Hz, Me); ^{13}C, δ 94.4 (C-1).

Anal. Calc. for $C_{13}H_{35}NO_7$: C, 69.77; H, 6.61; N, 2.63. Found: C, 69.94; H, 6.75; N, 2.48.

Concentration of the fractions containing the slower-moving product gave **1β** (65 mg, 4%) as an oil, $[\alpha]_D$ +93°. N.m.r. data: ^{1}H, δ 7.26 (Ph), 6.32 (d, $J_{1,2}$ 3.2 Hz, H-1), 1.92 (s, Ac*N*), 1.38 (d, *J* 7 Hz, Me); ^{13}C, δ 92.66 (C-1).

Anal. Found: C, 69.99; H, 6.71; N, 2.42.

1-O-(N-Acetyl-D-alanyl)-2,3,5-tri-O-benzyl-L-arabinofuranose (**2**). — To a solution of 2,3,5-tri-*O*-benzyl-β-L-arabinofuranose[5,7] (1.26 g), *N*-acetyl-D-alanine (400 mg), and imidazole (420 mg) in dichloromethane–*N,N*-dimethylformamide (10:1, 22 mL) was added dicyclohexylcarbodiimide (620 mg) and the reaction was continued as described above for **1**.

Column chromatography (solvent *D*) of the product mixture, followed by crystallisation from acetone–isopropyl ether–hexane, gave, as the faster-moving product, **2β** (16 mg, 1%), m.p. 106–114°, $[\alpha]_D$ +22°. N.m.r. data: ^{1}H, δ 7.30 (Ph), 6.29 (d, $J_{1,2}$ 3 Hz, H-1), 1.93 (s, Ac*N*), 1.26 (d, *J* 7 Hz, Me); ^{13}C, δ 95.37 (C-1).

Anal. Calc. for $C_{31}H_{35}NO_7$: C, 69.77; H, 6.61; N, 2.63. Found: C, 70.02; H, 6.83; N, 2.86.

The slower-moving product was **2α** (790 mg, 49%), m.p. 80–82°, $[\alpha]_D$ −30°. N.m.r. data: ^{1}H, δ 7.30 (Ph), 6.25 (s, H-1), 1.95 (s, Ac*N*), 1.30 (d, *J* 7 Hz, Me); ^{13}C, δ 101.41 (C-1).

Anal. Found: C, 69.92; H, 6.81; N, 2.60.

2,3,4-Tri-O-benzyl-1-O-(N-tert-butoxycarbonyl-L-phenylalanyl)-L-arabinopyranose (**3**). — To a solution of 2,3,4-tri-O-*benzyl*-β-L-arabinopyranose (2.1 g, 5 mmol) and imidazole (3.4 g, 50 mmol) in dichloromethane (20 mL) was added *N-tert*-butoxycarbonyl-L-phenylalanine pentachlorophenyl ester (2.55 g, 5 mmol), and the mixture was stirred for 2 h at room temperature. After work-up as described above, column chromatography (solvent *B*, 1:1) of the residue gave **3α,β** (2.23 g, 65%). Repeated chromatography (3 ×) gave, as the faster-moving fraction, **3β**, isolated as an oil (330 mg, 9.5%), $[\alpha]_D$ +76°. ^{1}H-N.m.r. data: δ 7.26 (Ph), 6.32 (d, $J_{1,2}$ 2.5 Hz, H-1), 1.40 (s, Me_3C).

Anal. Calc. for $C_{40}H_{45}NO_8$: C, 71.94; H, 6.79; N, 2.10. Found: C, 71.72; H, 6.60; N, 2.29.

Concentration of the slower-moving fractions afforded **3α** (1.9 g, 55%) as an oil, $[\alpha]_D$ 0°. N.m.r. data: ^{1}H, δ 7.26 (Ph), 5.71 (d, $J_{1,2}$ 4 Hz, H-1), 1.40 (s, Me_3C); ^{13}C, δ 93.96 (C-1).

Anal. Found: C, 71.65; H, 6.87; N, 2.10.

2,3,5-Tri-O-benzyl-1-O-(N-tert-butoxycarbonyl-L-phenylalanyl)-L-arabinofuranose (**4**). — 2,3,5-Tri-*O*-benzyl-β-L-arabinofuranose (840 mg), *N-tert*-butoxycarbonyl-L-phenylalanine pentachlorophenyl ester (1.03 g), and imidazole (1.36 g) were treated in dichloromethane (10 mL) as described above for **3**. Column chromatography of the crude product (solvent *B*, 1:1) gave **4α,β** (1.08 g, 80%). Two repetitions of the column chromatography (solvent *B*, 1:3) afforded the faster-moving **4α** (330 mg, 25%), m.p. 60–62° (from ethanol–water), $[\alpha]_D$ −17°. ^{1}H-

N.m.r. data: δ 7.26 (Ph), 6.22 (s, H-1), 3.03 (d, 2 H, *J* 6 Hz, PhCH_2), 1.40 (s, Me_3C).

Anal. Calc. for $C_{40}H_{45}NO_8$: C, 71.94; H, 6.79; N, 2.10. Found: C, 71.77; H, 7.01; N, 2.04.

From the slower-moving fractions, **4β** (190 mg, 14%) was isolated as an oil, $[\alpha]_D$ +37°. ^{1}H-N.m.r. data: δ 7.26 (Ph), 6.22 (d, $J_{1,2}$ 2 Hz, H-1), 2.90 (d, 2 Hz, PhCH_2), 1.38 (s, Me_3C).

Anal. Found: C, 71.97; H, 6.97; N, 2.25.

Catalytic hydrogenation of **3α**, **3β**, **4α**, *and* **4β**. — A solution of the 1-ester (100 mg) in dry ethyl acetate (10 mL) was shaken in an atmosphere of hydrogen in the presence of 10% Pd/C (100 mg) until hydrogen uptake was complete (4–6 h). The catalyst was removed, the filtrate was concentrated, and the residue (**5α**, **5β**, **6α**, or **6β**) was either acetylated or treated with diazomethane and then acetylated. Addition of pentane to the filtrate of the hydrogenation mixture of **3α** precipitated 1-*O*-(*N*-*tert*-butoxycarbonyl-L-phenylalanyl)-α-L-arabinopyranose (**5α**; 42 mg, 70%), m.p. 142–144°, $[\alpha]_D$ +13°. ^{1}H-N.m.r. data (C_5D_5N): δ 6.24 (d, $J_{1,2}$ 6.6 Hz), 1.39 (s, 9 H, Me_3C).

Anal. Calc. for $C_{19}H_{27}NO_8$: C, 57.41; H, 6.86; N, 3.52. Found: C, 57.64; H, 6.80; N, 3.33.

2,3,4-Tri-O-*acetyl-1*-O-(N-tert-*butoxycarbonyl*-L-*phenylalanyl*-α- (**7α**) *and* -β-L-*arabinopyranose* (**7β**). — (*a*) The crude product (**5α**) of the hydrogenation of **3α** was treated with acetic anhydride–pyridine (1:1, 4 mL) at room temperature for 4 h. The usual processing gave a syrupy product which contained (t.l.c.; solvent *B*, 5:2) mainly **7α** (R_F 0.5) and tetra-*O*-acetyl-L-arabinose (R_F 0.4). Column chromatography [solvent *B* (5:2) and then chloroform] of the mixture afforded **7α** (40 mg, 51%) as an oil, $[\alpha]_D$ +44°. ^{1}H-N.m.r. data: δ 7.26 (Ph); other data are given in Table I.

Anal. Calc. for $C_{25}H_{33}NO_{11}$: C, 57.35; H, 6.35; N, 2.68. Found: C, 57.17; H, 6.36; N, 2.54.

(*b*) Condensation of 2,3,4-tri-*O*-acetyl-L-arabinopyranose (710 mg) and *N*-*tert*-butoxycarbonyl-L-phenylalanine pentachlorophenyl ester (1.3 g) in dichloromethane (15 mL) in the presence of imidazole (1.7 g) was performed as described above for **3** to give, after column chromatography (solvent *B*, 5:2), **7α,β** (1.09 g, 81%).

Anal. Found: C, 57.17; H, 6.36; N, 2.54.

Repeated (6 ×) column chromatography of **7α,β** with chloroform gave **7α** (50 mg), identical with the product in (*a*), but the separation of **7β** from traces of **7α** was unsuccessful.

(*c*) The product (**5β**) of the hydrogenation of **3β** was acetylated as in (*a*). Column chromatography (chloroform) of the product gave **7β** (42 mg, 53%) as an oil, $[\alpha]_D$ +65°. The ^{1}H-N.m.r. data are given in Table I.

Anal. Found: C, 57.25; H, 6.50; N, 2.80.

2,3,5-Tri-O-*acetyl-1*-O-(N-tert-*butoxycarbonyl*-L-*phenylalanyl*)-α- (**8α**) *and*

-β-L-arabinofuranose (**8β**). — (*a*) The product (**6α**) of the hydrogenation of **4α** was acetylated and then purified by column chromatography (chloroform), as described above, to give **8α** (39 mg, 50%) as a glass, $[\alpha]_D$ −25°. The ^{1}H-n.m.r. data are given in Table I.

Anal. Calc. for $C_{25}H_{33}NO_{11}$: C, 57.35; H, 6.35; N, 2.68. Found: C, 57.17; H, 6.36; N, 2.54.

(*b*) The product (**6β**) of the hydrogenation of **4β** was treated as described in (*a*), to give **8β** (44 mg, 56%) as a glass, $[\alpha]_D$ +40°. For the ^{1}H-n.m.r. data, see Table I.

Anal. Found: C, 57.64; H, 6.50; N, 2.80.

*1,3,4(5)-Tri-*O*-acetyl-2-*O*-(*N*-tert-butoxycarbonyl-*L*-phenylalanyl)-*L*-arabinose* (**9**). — (*a*) A freshly prepared solution of the hydrogenation product (**5β**) of **3β** (100 mg) in dry *N,N*-dimethylformamide (1.50 mL) was treated with ethereal diazomethane (0.5 equiv.) at 0° for 1 h and then concentrated (0.1 Torr), and the residue was acetylated. Column chromatography (chloroform) of the product afforded a chromatographically homogeneous, viscous oil (42 mg, 53%). ^{1}H-N.m.r. data: δ 7.25 (Ph), 6.41 (d, ~0.3 H, $J_{1,2}$ 2.8 Hz, H-1 of β-L-Ara*p*), 6.19 (s, ~0.1 H, H-1 of α-L-Ara*f*), 5.68 (d, ~0.6 H, $J_{1,2}$ 7 Hz, H-1 of α-L-Ara*p*); other signals are given in Table I.

Anal. Calc. for $C_{25}H_{33}NO_{11}$: C, 57.35; H, 6.35; N, 2.68. Found: C, 57.64; H, 6.33; N, 2.67.

(*b*) The filtrate of the hydrogenation mixture of **3β** was treated with ethereal diazomethane (0.5 equiv.) at 0° for 1 h, and then processed as in (*a*) to give **9** (41 mg, 52%). ^{1}H-N.m.r. data: δ 7.25 (Ph), 6.41 (d, ~0.5 H, $J_{1,2}$ 2.8 Hz, H-1 of β-L-Ara*p*), 6.19 (s, ~0.1 H, H-1 of α-L-Ara*f*), 5.68 (d, ~0.4 H, $J_{1,2}$ 7 Hz, H-1 of α-L-Ara*p*); other signals are given in Table I.

(*c*) A solution of the hydrogenation product of **4β** in dry *N,N*-dimethylformamide (1.5 mL) at 0° was kept thereat for 1 h. Processing as in (*a*) then gave **9** (39 mg, 50%). ^{1}H-N.m.r. data: δ 7.25 (Ph), 6.41 (d, ~0.3 H, 2.8 Hz, H-1 of β-L-Ara*p*), 6.19 (s, ~0.1 H, H-1 of α-L-Ara*f*), 5.68 (d, ~0.6 H, $J_{1,2}$ 7 Hz, H-1 of α-L-Ara*p*); other signals are given in Table I.

(*d*) Treatment of the filtrate of the hydrogenation mixture of **6β** with ethereal diazomethane, and processing as in (*b*), gave **9** (40 mg, 52%). ^{1}H-N.m.r. data: δ 7.25 (Ph), 6.41 (d, ~0.45 H, $J_{1,2}$ 2.8 Hz, H-1 of β-L-Ara*p*), 6.22 (d, ~0.06 H, $J_{1,2}$ 2 Hz, H-1 of β-L-Ara*f*), 6.14 (s, ~0.13 H, H-1 of α-L-Ara*f*), 5.68 (d, ~0.35 H, $J_{1,2}$ 7 Hz, H-1 of α-L-Ara*p*); other signals are given in Table I.

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