Carbohydrate Research, 138 (1985) 41–54
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

1,2-*O*-CYANOALKYLIDENE DERIVATIVES OF FURANOSES AS 1,2-*trans*-GLYCOSYLATING AGENTS

LEON V. BACKINOWSKY, SERGEI A. NEPOGOD'EV, ALEXANDER S. SHASHKOV, AND NIKOLAY K. KOCHETKOV

N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

(Received, June 14th, 1984; accepted for publication, September 17th, 1984)

ABSTRACT

Treatment of acetylated L-arabinofuranose, D-galactofuranose, and D-glucofuranose with trimethylsilyl cyanide in acetonitrile in the presence of stannous chloride gave the respective 1,2-*O*-(1-cyanoethylidene) derivatives. Triphenylmethylium perchlorate-catalysed glycosylation of trityl ethers of monosaccharides by the above cyanoethylidene derivatives and by 3,5-di-*O*-benzoyl-1,2-*O*-(α-cyanobenzylidene)-β-L-arabinofuranose gave high yields of protected disaccharides containing a 1,2-*trans*-glycofuranosidic bond.

INTRODUCTION

1,2-*O*-(1-Cyanoethylidene) derivatives of hexopyranoses have found application in syntheses of oligo- and poly-saccharides as effective 1,2-*trans*-glycosylating agents[1]. A characteristic feature of these glycosylation reactions is their high stereoselectivity, which is independent of the nature of the glycosylating component. With the aim of extending the scope of this glycosylation method, we have synthesised the 1,2-*O*-(1-cyanoethylidene) derivatives of L-arabino-, D-galacto-, and D-gluco-furanoses, and have studied their glycosylating properties.

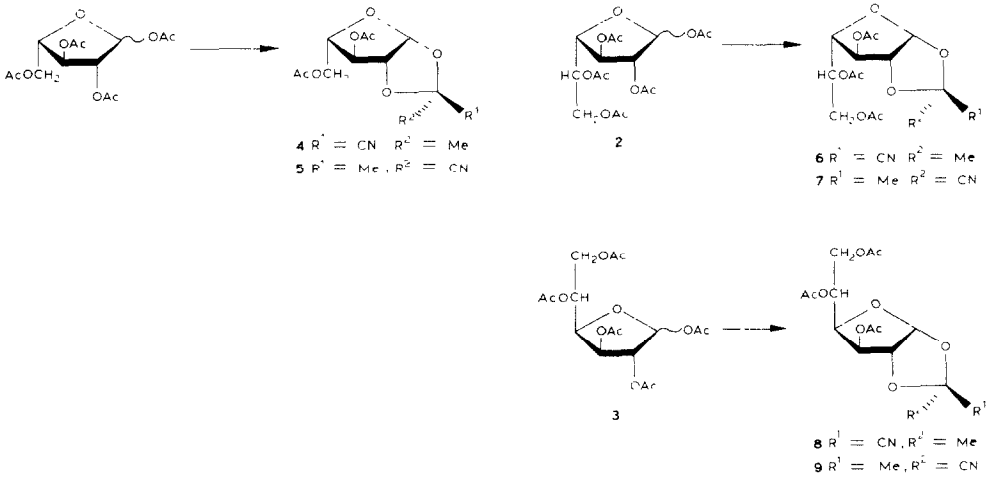
RESULTS AND DISCUSSION

*Synthesis of 1,2-*O*-(1-cyanoethylidene) derivatives.* — The known procedures for preparing sugar 1,2-*O*-(1-cyanoethylidene) derivatives involve interaction of acetylglycosyl bromides with sodium or potassium cyanide in acetonitrile at room temperature[2–4] or with silver cyanide in boiling xylene[5–7]. Recently, it was shown that treatment of β-D-ribofuranose tetra-acetate with trimethylsilyl cyanide in the presence of a Lewis acid can give the 1,2-*O*-(1-cyanoethylidene) derivative of D-ribofuranose[8]. We have studied the applicability of this reaction for preparing the cyanoethylidene derivatives of other furanoses. Therefore, we have synthesised the acetylated L-arabino-, D-galacto-, and D-gluco-furanoses (**1–3**) as starting products.

α,β-L-Arabinofuranose tetra-acetate (**1**) was obtained by the procedure used

0008-6215/85/$ 03.30

to prepare 1,2,3,5-tetra-*O*-acetyl-D-ribofuranose[9]. The ^{13}C-n.m.r. spectrum of **1** coincided with that published for the D enantiomer[10]. Acetylation of D-galactose at elevated temperature[11] gave a mixture of pyranose and furanose penta-acetates. The α,β-furanose derivative **2** was isolated by column chromatography of the mother liquor after crystallisation of β-D-galactopyranose penta-acetate. The synthesis of **3** involved deacetonation of the known 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose[12,13] by using aqueous 90% trifluoroacetic acid[14] followed by acetylation.



The ^{13}C-n.m.r. spectra of **1–3** exhibited, *inter alia*, low-field signals at δ ~80 characteristic for C-4 of furanose derivatives, and two sets of signals corresponding to α and β anomers. Assignment of the signals in the spectrum of **2** was made by analogy with the data for **1** (the configurational similarity of the pairs α-L-Ara*f*/β-D-Gal*f* and β-L-Ara*f*/α-D-Gal*f* being taken into account) and for D-galactofuranose α- and β-pentabenzoates[15]. Assignment of the signals in the spectrum of **3** was made with the use of data for D-xylofuranose α- and β-tetra-acetates[10].

The synthesis of 1,2-*O*-(1-cyanoethylidene) derivatives was carried out under conditions somewhat different from those described[8]. The acetates **1–3** were each treated with 2.5 equiv. of trimethylsilyl cyanide in dry acetonitrile in the presence of 0.2 equiv. of stannous chloride at room temperature. The diastereomeric cyanoethylidene derivatives **4/5, 6/7,** and **8/9** were isolated by column chromatography.

The structures of **4–9** were established on the basis of n.m.r. data (Tables I–III). The presence of the high-field ^{1}H signal for the methyl group (δ 1.77–1.93) and the ^{13}C signals for the methyl group (δ 24–27), the cyano group (δ 116–117), and the quaternary carbon atom (δ 100–102) indicate the presence of the cyanoethylidene group. The low-field signals for C-4 were characteristic of the furanose form. The 1,2-fusion of the dioxolane ring was evidenced by the low-field

TABLE I

^{1}H-N M.R CHEMICAL SHIFTS (δ, p.p.m.) FOR THE 1,2-*O*-CYANOALKYLIDENE DERIVATIVES **4–10**

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*	*H-6*	*H-6'*	*OAc*	*CCH$_3$*
4	6.14	4.86	5.15	4.41	4.27	4.15			2.09 2.10	1.88
5	5.96	4.80	5.26	4.09	4.52	4.32			2.11 2.13	1.81
6	6.11	4.89	5.21	4.30	5.28		4.42	4.11	2.06 2.11 2.13	1.93
7	5.89	4.78	5.24	4.03	5.30		4.39	4.22	2.05 2.12 2.16	1.82
8	6.13	4.73	5.42	4.33	5.25		4.56	4.10	2.02 2.08 2.09	1.85
9	6.08	4.60	5.55	4.91	5.18		4.52	4.20	2.03 2.07 2.09	1.77
10[a]	6.48	5.27	5.59	4.74	4.32–4.45					

[a]Aromatic protons: δ 8.08–8.01 and 7.75–7.35.

TABLE II

VICINAL PROTON–PROTON COUPLING CONSTANTS (Hz) FOR COMPOUNDS **4–10**

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
4	4.2	0	1.1	7.3	7.1	11.6			
5	4.0	2.3	6.9	3.5	6.2	12.2			
6	4.1	0	1.1	9.3			3.7	5.6	12.0
7	4.3	2.3	8.0	3.3			4.9	6.5	11.5
8	3.9	0	2.9	9.2			2.3	5.4	12.2
9	3.6	0	3.3	9.2			2.1	4.0	12.2
10	4.2	0	1.1	7.0	7.0	12.5			

TABLE III

^{13}C-N M R CHEMICAL SHIFTS (δ, p.p.m.) FOR THE 1,2-*O*-CYANOALKYLIDENE DERIVATIVES **4–10**

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*CN—C—CH$_3$*		
4	107.0	85.5	76.7	85.2	63.0		116.4	100.6	24.55
5	104.6	87.9	75.6	79.25	62.6		117.7	100.6	26.0
6	106.5	85.8[a]	75.9	85.5[a]	69.7	62.8	116.5	101.2	24.1
7	104.0	88.0	74.4	78.4	68.1	62.6	117.5	100.9	26.3
8	105.7	84.3	73.6	77.7	67.0	63.1	116.5	100.2	24.55
9	106.4	85.6	73.55	78.75	67.7	62.8	117.7	102.0	27.2
10	107.2	86.1	77.1	85.4	63.7		116.2	102.8	

[a]Assignments may be interchanged. Other signals: CH_3CO, 170.3–169.2; Ph*C*O, 165.9–165.2; Ph, 133.9–125.9; *C*H$_3$CO, 20.8–20.55 p.p.m.

signals for H-3 and high-field signals for H-2, whereas the *cis*-fusion followed from the characteristic[16,17] $J_{1,2}$ values (3.6–4.3 Hz).

The chemical shifts of the ^1H signals for the methyl group and the ^{13}C signals for the methyl and cyano groups for the pairs of diastereomers differ in similar fashion. This allows the stereochemistry at C-2 of the dioxolane ring to be assigned as *endo*-methyl for **4, 6,** and **8,** and *exo*-methyl for **5, 7,** and **9,** by analogy with the 1,2-*O*-(1-cyanoethylidene) derivatives of hexopyranoses, where the ^1H signal for the *endo*-CH_3 is downfield[2,18] compared with that for *exo*-CH_3. The ^3J data for **4–7** (Table II) suggest a conformation close to ^1E for **4** and **6** and close to E_0 for **5** and **7**. The values of $J_{1,2}$, $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ for **8** and **9** are similar (and close to those for 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose to which the $^3T_2$ conformation was assigned[16]), thus pointing to a similarity of their conformations.

A regular pattern was observed for the $[\alpha]_D$ values of **4–9**. The *endo*-cyano isomers **5, 7,** and **9** are more dextrorotatory than the respective *exo*-cyano isomers.

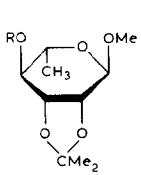
The spectral characteristics of the 1,2-*O*-(1-cyanoethylidene) furanose derivatives allowed the determination of the configuration of C-2 of the dioxolane ring of the known[2] 3,5-di-*O*-benzoyl-1,2-*O*-(α-cyanobenzylidene)-β-L-arabinofuranose (**10**). On the basis of identical $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ values for **10** and **4**, and the similar chemical shifts for C-1, C-4, and the cyano group, the *exo*-cyano configuration is assigned to **10**.

Synthesis of glycofuranosides. — The cyanoalkylidene derivatives **4–10** were used to glycosylate the following trityl ethers: methyl 2,3-*O*-isopropylidene-4-*O*-trityl-α-L-rhamnopyranoside[19] (**11**), 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl-β-D-glucopyranose[20] (**12**), methyl 2,3-di-*O*-acetyl-5-*O*-trityl-α-L-arabinofuranoside[21] (**13**), methyl 3,5-di-*O*-acetyl-2-*O*-trityl-α-L-arabinofuranoside (**14**), methyl 2,5-di-*O*-acetyl-3-*O*-trityl-α-L-arabinofuranoside (**15**), and 4-*O*-acetyl-1,2,5,6-tetra-*O*-benzoyl-3-*O*-trityl-D-mannitol (**18**).

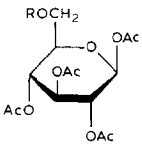
The trityl ethers **14** and **15** were prepared from methyl α-L-arabinofuranoside by reaction with 2 mol of acetic anhydride and tritylation of the resulting mixture of diacetates using triphenylmethylium perchlorate[19]. The isomers were isolated by column chromatography and their structures were assigned on the basis of a comparison of the chemical shifts of the H-3 signals. Tritylation of the known[22] 1,2,5,6-tetra-*O*-benzoyl-D-mannitol (**16**) followed by acetylation of the product (**17**) in the presence of 4-dimethylaminopyridine gave **18**.

The glycosylation reactions were carried out[19] in dichloromethane in the presence of 0.1 equiv. of triphenylmethylium perchlorate as the catalyst, and the products were isolated by column chromatography.

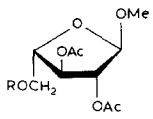
The disaccharide derivatives **19–24** and **31** were obtained both from *exo*- and *endo*-cyanoethylidene derivatives in almost equal yields, indicating that the glycosylating activity of the 1,2-*O*-cyanoethylidene derivatives of furanoses is independent of the configuration at C-2 of the dioxolane ring, as found for the analogous derivatives of hexopyranoses[19] and xylopyranose[3]. All the glycosylation reactions proceeded stereospecifically to give 1,2-*trans*-furanosides only. The prop-



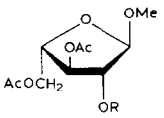
11 R = Tr
19 R = $AraAc_3$
20 R = $AraBz_3$
25 R = $GalAc_4$
26 R = $GlcAc_4$



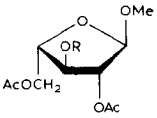
12 R = Tr
21 R = $AraAc_3$
22 R = $AraBz_3$



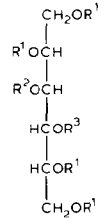
13 R = Tr
23 R = $AraAc_3$
24 R = $AraBz_3$



14 R = Tr
27 R = $AraAc_3$
28 R = $AraBz_3$

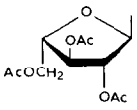


15 R = Tr
29 R = $AraAc_3$
30 R = $AraBz_3$

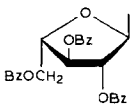


16 R^1 = Bz, R^2 = R^3 = H
17 R^1 = Bz, R^2 = Tr, R^3 = H
18 R^1 = Bz, R^2 = Tr, R^3 = Ac
31 R^1 = Bz, R^2 = $GalAc_4$, R^3 = Ac
32 R^1 = R^3 = H, R^2 = Gal

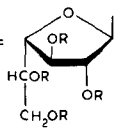
$AraAc_3$ =



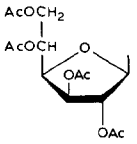
$AraBz_3$ =



$GalAc_4$(R = Ac) =
Gal (R = H) =



$GlcAc_4$ =



erties of **19–24** and of the galactofuranosylmannitol **32** (obtained by deacylation of **31**) were in close agreement with those reported[21,23]. The products present in the mother liquors after crystallisation of the disaccharide derivatives **20, 21,** and **29** were homogeneous in t.l.c. and their $[\alpha]_D$ values were almost identical to those of the corresponding crystalline samples.

The structures of all the disaccharide derivatives obtained were established on the basis of n.m.r. data (Tables IV–VI). The ^1H- and ^{13}C-n.m.r. spectra were interpreted with the aid of homonuclear $^1H\{^1H\}$ and selective heteronuclear $^1H\{^{13}C\}$ double resonances and by reference to the data for methyl 2,3,5-tri-*O*-acetyl-α-L-arabinofuranoside[24] (**33**) and methyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranoside[25] (**34**).

In the ^1H-n.m.r. spectra, the signal for H-1 of each glycosylating furanose residue was a slightly broadened singlet ($J_{1,2}$ and $J_{1,3}$ ≤0.5 Hz), indicating a 1,2-*trans*-configuration of the furanosidic bond[10,26]. For **19–24** and **27–30**, the signal for

TABLE IV

^{1}H-N M R CHEMICAL SHIFTS (δ, p.p.m.) FOR THE DISACCHARIDE (**19–30**) AND MONOSACCHARIDE (**33, 34**) DERIVATIVES

Compound	*Residue*[a]	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*	*H-6*	*H-6'*	*CH_3O*	*AcO*
19	N	5.56	5.12	4.96	4.29	4.19[b]	4.38				2.12, 2.09 (×2)
	R	4.87	4.10	[b]	3.72	3.54[c]		1.26		3.37	
20	N	5.82	5.62	5.56	4 61	4.71	4.82				
	R	4.89	4.12	4.30	3.67	3.80[b]		1.32		3.37	
21	N	4.98	[b]	4.92	4.23	4.17	4.35				2 07, 2.09 (×3),
	R	5.64	[b]	5.19	5.06–4 99[b]	3.80		3 73	3.57		1.98, 1.96, 1.94
22	N	5.32	5.55	5.58	4.77	4.64[b]	4.98				
	R	5.73	5.11	5.29	5.17	4.00–3.88[c]		[c]	3.73		2.03, 2.01, 1.99, 1.89
23	N	5.16	5.17	4.95	4 33	4.15[b]	4.46[d]				
	R	4.93	5.05	5.19	[b]	3.76	3 95			3 40	2 10 (×5)
24	N	5.42	5.63	5.61	4 75	4.66[b]	4 88[d]				
	R	4.95	5.10	5.25	4.25	3.90	4.08			3.37	2.05, 1.99
25	N	5.56	5.07	5.00	[b]	5.39		4.32	4.25–4.16[b]		2.13, 2.12, 2 08, 2.06
	R	4.86	4.09	[b]	3.53	3.67		1.26		3.38	
26	N	5.52	5.08	5.37	4.52	5.28		4.61	4 21–4.14[b]		2.13, 2.09, 2.04, 1.99
	R	4.86	4.09	[b]	3.54	3 64		1.33		3.37	
27	N	5.33	5.08	5.02	4.29	4.19[b]	4.45–4 36[c]				
	R	5.00	4.18	4.94	[b]		[c]			3 40	2.12(×2), 2.10(×3)
28	N	5.61	5.54	5.62	4.60	4 71	4.82				
	R	5.09	[b]	5.05	4.32	4.24[b]	4.48[d]			3 39	2.10 (×2)
29	N	5.28	5.15	4.99	4.26	4.17[b]	4.44–4.35[c]				
	R	4.93	5.03	4.03	[b]		[c]			3.41	2.12–2.10(×5)
30	N	5.64	5.67	5.65	4.67	4 75	4.89				
	R	5.03	5.21	4.24	4.41	4.33[b]	4.50[d]			3.48	2.17, 2.11
33		4 94	5 07	4.99	4.27	4.19[b]	4.45[d]			3 41	2.11 (×3)
34		5.19	5.53	5.60	4.58	4.70	4.86			3.50	

[a]N, non-reducing end; R, "reducing" end. [b,c]Multiplet. [d]Centre of a multiplet Other signals: aromatic protons, δ 8 17–7.97 and 7.70–7.23; isopropylidene methyl groups, δ 1.56–1.54 and 1.34–1.32.

TABLE V

VICINAL PROTON–PROTON COUPLING CONSTANTS (Hz) FOR COMPOUNDS **19–30, 33,** AND **34**

Compound	*Residue*[a]	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
19	N	1.3	3.4	—	—	—			
	R	5.3	6.6	9.5			5.3		
20	N	1.0	4.4	5.2	3.6	11.1			
	R	5.3	6.5	—			5.3		
21	N	1.5	4.7	5.0	2.7	10.6			
	R[b]	—	9.0	9.4			2.5	5.3	11.1
22	N	1.0	4.2	—	—	—			
	R[c]	9	9	9			—	—	—
23	N	1.3	4.0	—	—	—			
	R	1.7	5.0	2.5	3.5	10.4			
24	N	1.0	4.2	—	—	—			
	R	1.6	5.0	2.5	3.9	10.5			
25	N	1.7	5.2	3.9			4.9	6.9	11.5
	R	5.5	7.2	9.8			6.0		
26	N	0	4.7	9.7			2.5	4.8	11.5
	R	5.6	6.8	9.8			6.0		
27	N	1.7	5.0	—	—	—			
	R	1.3	4.0	—	—	—			
28	N	1.4	4.2	4.9	3.7	11.8			
	R	—	4.2	—	—	—			
29	N	1.8	5.0	—	—	—			
	R	1.8	5.8	—	—	—			
30	N	1.2	4.3	5.2	3.6	11.8			
	R	1.6	5.8	—	—	—			
33[d]		1.6	4.5	—	—	—			
34[e]		1.4	5.1	4.7	3.5	11.9			

[a]N, non-reducing end; R, "reducing" end. [b]$J_{1,2}$ 7.7 Hz. [c]$J_{1,2}$ 8.0 Hz. [d]$J_{1,2}$ 0.5, $J_{1,3}$ 0.6 Hz. [e]$J_{1,2}$ 0.2, $J_{1,3}$ 0.7 Hz. All other H-1 signals are singlets.

H-1′ was shifted to lower field in comparison with those of the methyl arabinofuranosides **33** and **34**. Interpretation of the ^{1}H-n.m.r. spectra was facilitated by the facts that the chemical shifts of the signals of the protons of the aglycons were practically independent of the nature of the glycosylating moiety and that substitution of acetyl for benzoyl groups in the latter resulted in a downfield shift not only of the signals for H-2′, H-3′, and H-5′, but also of those for H-1′ and H-4′.

There was only one ^{13}C signal in the furanoside C-1 region for **19–22, 25,** and **26**. Two signals due to C-1 and C-1′ were observed in the analogous region for **23, 24,** and **27–30,** those for C-1′ being at δ 106.1–105.1 and those for C-1 being at δ 108.1–106.7.

The n.m.r. data allowed the substitution pattern in **25–30** to be established, since H-2 in **27** and **28** and H-3 in **29** and **30** resonate at higher field ($\Delta\delta \sim 1$ p.p.m.) and C-2 and C-3 at lower field (due to the α-effect of glycosylation) than the corresponding atoms in the glycosides **33** and **34**. The location of the glycosyl residues in **25** and **26** was indicated by the downfield shift of the signal for C-4 of the rhamnose

TABLE VI

^{13}C-N M R CHEMICAL SHIFTS (δ, p.p.m.) FOR THE DISACCHARIDE (**19–30**) AND MONOSACCHARIDE (**33,34**) DERIVATIVES

Compound	*Residue*[a]	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*OCH_3*
19	N	104.1	81.0	77.6	81.0	63.6		
	R	98.2	76.1	78.25	76.5	64.0	17.6	54.8
20	N	104.3	81.95	78.35	81.6	64.2		
	R	98.1	76.05	78.15	76.7	64.0	17.8	54.8
21	N	106.05	81.2	77.0	80.4	63.2		
	R	91.7	70.35	72.9	68.6	74.0	65.9	
22	N	106.3	81.9	77.65	81.5	63.8		
	R	91 75	70.4	73.2	68.65	73.9	66.1	
23	N	105.7	81.0	77.4	80.9	63.3		
	R	106.8	82.0	76.75	81.0	65.7		54.85
24	N	106.05	81.9	77.9	81.3	63.7		
	R	106.7	81.8	77.0	81.2	66.1		54 7
25	N	103.8	81.2	76.7	80.6	69.4	62.4	
	R	98.1	76.05	78.1	76.6	63.8	17.65	54.8
26	N	104.55	80.0	73.2	78.85	68.4	63.35	
	R	98.0	76.0	77.9	77.1	64.0	17 5	54.8
27	N	105.1	81.6	77.1	80.8	63.2[b]		
	R	108.0	84.5	77.7	80.4	63.7[b]		54.9
28	N	105.4	82.3	77.9	81.7	63.75		
	R	108.1	84.9	78.0	80.4	63.9		54.9
29	N	105.15	81.1	77.1	80.2[b]	63.2		
	R	107.1	82.0	80.8	80.8[b]	63.2		54.9
30	N	105.6	81.8	77.8	81.9	63.9		
	R	107 1	82.1	81.35	80 65	63.25		54.85
33		106.85	81.35	77.25	80.3	63.35		55.0
34		106.95	82.25	78.0	80.9	63.8		55.0

[a]N, non-reducing end; R, "reducing" end. [b]Assignments may be interchanged. Other signals: CH_3CO, 170.1–168.8; Ph*C*O, 166.2–165.3; Ph, 133.5–128.3; $C(CH_3)_2$, 109.5; CH_3CO, 20.8–20.5; $C(CH_3)_2$, 27.9 and 26.4 p.p.m.

residues. The observed α-effect of glycosylation ($\Delta\delta$ 1.9–2.5 p.p.m. in comparison with the chemical shift of the signal for C-4 in methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside[27]) is less than for glycosylation by pyranoid moieties ($\Delta\delta$ 4–6 p.p.m.)[3,7,27]. Analogous differences were observed for the signal of C-6 of the glucose residue in **21** and **22** (*cf.* refs. 7 and 27).

The ready accessibility of 1,2-*O*-cyanoalkylidene furanose derivatives and the stereospecific glycosylation effected provides a convenient route to synthesis of 1,2-*trans*-glycofuranosides.

EXPERIMENTAL

Pyridine and 2,4,6-trimethylpyridine were distilled from KOH and then from CaH_2. Acetonitrile was dried with $CaCl_2$, and distilled from $CaCl_2$ and then from CaH_2. Dichloromethane was washed with conc. H_2SO_4 and water, dried with

$CaCl_2$, and distilled from CaH_2. Nitromethane was distilled from urea at 100mmHg, then from P_2O_5, and finally from CaH_2. Benzene was distilled from sodium. Triphenylmethylium perchlorate was synthesised as described[28], and further purified[4] when used as a catalyst for glycosylation. Optical rotations for solutions in chloroform (unless otherwise stated) were measured with a Perkin–Elmer 141 polarimeter at 22 ±2° and melting points with a Kofler apparatus. N.m.r. spectra were recorded with a Bruker WM-250 instrument for solutions in $CDCl_3$ (internal Me_4Si). Column chromatography was performed on silica gel L 40/100 μm (CSSR) and t.l.c. on Kieselgel 60 (Merck) with detection by charring with sulphuric acid. The following solvent systems were used: *A*, 3:2 benzene–ether; *B*, 3:1 chloroform–acetone; and *C*, 9:1 benzene–ethyl acetate. Column chromatography was performed with *D*, benzene; and *E*, a benzene→ether gradient. Solutions were concentrated *in vacuo* at 40°.

*1,2,3,5-Tetra-*O*-acetyl-α,β-*L*-arabinofuranose* (**1**). — A mixture of dry L-arabinose (10 g) and dry methanol (200 mL) was treated with methanolic 1.06M hydrogen chloride [prepared by the addition, at 0°, of acetyl chloride (4.7 mL) to dry methanol (63 mL)], and the mixture was agitated at 0–5° overnight. Pyridine (40 mL) was added to neutralise the mixture which was then concentrated, and pyridine was distilled from the residue several times. The residue was dissolved in pyridine (80 mL), acetic anhydride (30 mL) was added with cooling, and the solution was left at room temperature for 2 days. Conventional work-up gave a syrupy product which was dissolved in a mixture of acetic acid (100 mL) and acetic anhydride (25 mL), conc. H_2SO_4 (5 mL) was added at 0°, and the mixture was left overnight at room temperature. The solution was poured onto crushed ice (150 g), and the mixture was stirred for 2 h and extracted with chloroform. The extract was washed with water and aqueous sodium hydrogencarbonate, and concentrated, and the residue was subjected to column chromatography (solvent *E*) to give syrupy **1** (18.0 g, 85%), R_F 0.46 (solvent *A*). ^{13}C-N.m.r. data: δ 170.25–169.2 (CH_3CO), 99.4 (C-1α), 93.7 (C-1β), 82.6 (C-4α), 80.6 (C-2α), 79.8 (C-4β), 76.9 (C-3α), 75.4 (C-2β), 74.9 (C-3β), 64.5 (C-5β), 63.1 (C-5α), 20.6 (CH_3CO).

*1,2,3,5,6-Penta-*O*-acetyl-α,β-*D*-galactofuranose* (**2**). — D-Galactose was acetylated according to Ness *et al.*[11]. Crystallisation of the product from ethanol gave 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose, m.p. 142–144°, $[\alpha]_D$ +28° (*c* 1.5); lit.[11] m.p. 143–144° (from ethanol), $[\alpha]_D$ +27.4° (chloroform). The mother liquor was concentrated and column chromatography of the residue (1:2 benzene–ether) gave **2** as a syrup (14%), $[\alpha]_D$ +40°– +50°, R_F 0.34 (solvent *A*). ^{13}C-N.m.r. data: δ 170.4–169.4 (CH_3CO), 99.2 (C-1β), 93.2 (C-1α), 82.2 (C-4β), 80.7 (C-2β), 79.25 (C-4α), 76.4 (C-3β), 75.4 (C-2α), 73.7 (C-3α), 70.5 (C-5α), 69.4 (C-5β), 62.6 (C-6β), 62.2 (C-6α), 21.0–20.4 (CH_3CO).

*1,2,3,5,6-Penta-*O*-acetyl-α,β-*D*-glucofuranose* (**3**). — A solution of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose[12,13] (3.5 g, 10 mmol) in aqueous 90% trifluoroacetic acid (15 mL) was kept for 1 h at room temperature and then concentrated to dryness, and the residue was subjected to column chromatography

(solvent *B*) to give a syrupy product, $[\alpha]_D$ +22°→+26.5° (1 h, *c* 2.2), R_F 0.31 (solvent *B*). A solution of this product in 3:1 pyridine–acetic anhydride (8 mL) was left for 1 h at room temperature. Ethanol (1 mL) was then added and, after 30 min, the solution was concentrated. Column chromatography (solvent *E*) of the residue yielded **3** (2.7 g, 70%) as a syrup, $[\alpha]_D$ +45° (*c* 1.75), R_F 0.37 (solvent *A*). ^{13}C-N.m.r. data: δ 170.5–168.9 (CH_3CO), 99.0 (C-1β), 94.0 (C-1α), 79.8 (C-2β, C-4β), 76.8, 76.5 (C-2α, C-4α), 74.1, 73.1 (C-3α, C-3β), 68.4, 68.0 (C-5α, C-5β), 63.1, 62.8 (C-6α, C-6β), 21.0–20.3 (CH_3CO).

*3,5-Di-*O*-acetyl-1,2-*O*-[(1-*exo*- and 1-*endo*-cyano)ethylidene]-β-*L*-arabinofuranoses* (**4** *and* **5**). — To a solution of **1** (3.0 g, 9.43 mmol) in acetonitrile (10 mL) were added anhydrous stannous chloride (360 mg, 1.89 mmol) and trimethylsilyl cyanide (3.0 mL, 23.6 mmol). The mixture was stirred overnight at room temperature (formation of appreciable amounts of **4** and **5** was detected by t.l.c. after 1–2 h), diluted with ether (100 mL), and then washed with aqueous sodium hydrogencarbonate (3 × 75 mL) and water. The organic layer was concentrated and the residue was subjected to column chromatography (solvent *E*) to give **4** (994 mg, 37%) and **5** (700 mg, 26%). Crystallisation from ether–pentane gave the *exo*-cyano isomer **4** (35%), m.p. 66–69°, $[\alpha]_D$ −6° (*c* 1), R_F 0.56 (solvent *A*). Crystallisation from toluene gave the *endo*-cyano isomer **5** (23%), m.p. 107–110°, $[\alpha]_D$ +51° (*c* 1), R_F 0.37.

Anal. Calc. for $C_{12}H_{15}NO_7$: C, 50.52; H, 5.31; N, 4.91. Found for **4**: C, 50.88; H, 5.50; N, 4.72. Found for **5**: C, 50.66; H, 5.42; N, 4.67.

*3,5,6-Tri-*O*-acetyl-1,2-*O*-[(1-*exo*- and 1-*endo*-cyano)ethylidene]-α-*D*-galactofuranoses* (**6** *and* **7**). — These compounds, prepared from **2** using the procedure described above, were obtained in a ratio of ~6:5 (combined yield, 66%). The *exo*-cyano isomer **6** had m.p. 78–80° (from ether), $[\alpha]_D$ −4° (*c* 1.3), R_F 0.47 (solvent *A*). The *endo*-cyano isomer **7** had m.p. 78–80° (from ether), $[\alpha]_D$ +78° (*c* 1.4), R_F 0.29.

Anal. Calc. for $C_{15}H_{19}NO_9$: C, 50.42; H, 5.36; N, 3.92. Found for **6**: C, 50.89; H, 5.28; N, 4.24. Found for **7**: C, 50.75; H, 5.60; N, 3.79.

*3,5,6-Tri-*O*-acetyl-1,2-*O*-[(1-*exo*- and 1-*endo*-cyano)ethylidene]-α-*D*-glucofuranoses* (**8** *and* **9**). — Starting from **3**, the title compounds were prepared, as described above, in the ratio 2:1 (total yield, 82%); the *exo*-cyano isomer **8** had m.p. 83.5–85.5° (from ethanol), $[\alpha]_D$ +9° (*c* 2), R_F 0.58 (solvent *A*); the *endo*-cyano-isomer **9** had m.p. 116–118° (from toluene–hexane), $[\alpha]_D$ +57° (*c* 2.1), R_F 0.44.

Anal. Calc. for $C_{15}H_{19}NO_9$: C, 50.42; H, 5.36; N, 3.92. Found for **8**: C, 50.60; H, 5.25; N, 3.84. Found for **9**: C, 50.28; H, 5.43; N, 3.52.

*Methyl 3,5-di-*O*-acetyl-2-*O*-trityl-α-*L*-arabinofuranoside* (**14**) *and methyl 2,5-di-*O*-acetyl-3-*O*-trityl-α-*L*-arabinofuranoside* (**15**). — A solution of acetic anhydride (3.5 mL, 37 mmol) in dry chloroform (30 mL) was added dropwise, at 0°, to a solution of methyl α-L-arabinofuranoside[21] (3.0 g, 18.5 mmol; prepared from the corresponding crystalline tribenzoate **34**[25]) in pyridine (20 mL). The solution was kept at 10° for 5 h, treated with ethanol (1 mL), and, after 0.5 h, diluted with

chloroform (150 mL) and washed with water (3 × 50 mL). The organic layer was concentrated, the residue was dried *in vacuo*, and a solution in dichloromethane (50 mL) containing 2,4,6-trimethylpyridine (1.32 mL, 10 mmol) was treated with triphenylmethylium perchlorate (3.1 g, 9 mmol) portionwise during 30 min with stirring. After 3 h, the mixture was diluted with chloroform (100 mL), washed with water (3 × 50 mL), and concentrated. Column chromatography of the residue gave **14** (14%) and **15** (10%).

Compound **14** had m.p. 130–131° (from ether–pentane), $[\alpha]_D$ −23.5° (*c* 1.15), R_F 0.36 (solvent *C*). N.m.r. data: ^1H, δ 7.46–7.21 (m, 15 H, 3 Ph), 4.93 (bd, 1 H, $J_{2,3}$ 1.1, $J_{3,4}$ 4.2 Hz, H-3), 4.48 (dd, 1 H, $J_{4,5}$ 3.4, $J_{5,5'}$ 11.4 Hz, H-5), 4.27 (dd, 1 H, $J_{4,5'}$ 5.9 Hz, H-5'), 4.19 (d, 1 H, H-2), 3.99 (m, 1 H, H-4), 3.98 (s, 1 H, H-1), 3.03 (s, 3 H, OMe), 2.13 (s, 3 H, AcO), 1.99 (s, 3 H, AcO); ^{13}C, δ 169.9 (CH_3CO), 143.7, 128.95, 128.0, 127.4 (aromatic), 108.0 (C-1), 88.6 (Ph_3C), 82.8 (C-2), 80.8 (C-4), 79.55 (C-3), 64.05 (C-5), 54.7 (OCH_3), 20.9, 20.8 (CH_3CO).

Compound **15** had m.p. 129–130° (from ether–pentane), $[\alpha]_D$ −73° (*c* 1.7), R_F 0.31. N.m.r. data: ^1H, δ 7.49–7.14 (m, 15 H, 3 Ph), 4.69 (s, 1 H, H-1), 4.45 (ddd, 1 H, $J_{3,4}$ 4.6, $J_{4,5}$ 2.8, $J_{4,5'}$ 6.8 Hz, H-4), 4.34 (d, 1 H, $J_{2,3}$ 0.8 Hz, H-2), 4.16 (dd, $J_{5,5'}$ 11.9 Hz, H-5), 3.97 (bd, 1 H, H-3), 3.74 (dd, 1 H, H-5'), 3.42 (s, 3 H, OMe), 2.02 (s, 3 H, AcO), 1.83 (s, 3 H, AcO); ^{13}C, δ 170.6, 169.1 (CH_3CO), 143.95, 129.1, 128.0, 127.5 (aromatic), 107.2 (C-1), 88.05 (Ph_3C), 82.1 (C-4), 81.8 (C-2), 78.3 (C-3), 63.9 (C-5), 54.8 (OCH_3), 20.8, 20.5 (CH_3CO).

Anal. Calc. for $C_{29}H_{30}O_7$: C, 71.00; H, 6.16. Found for **14**: C, 71.03; H, 6.33. Found for **15**: C, 70.88; H, 6.29.

1,2,5,6-Tetra-O-benzoyl-3-O-trityl-D-mannitol (**17**). — Triphenylmethylium perchlorate (3.43 g, 10 mmol) was added portionwise with stirring to a solution of 1,2,5,6-tetra-*O*-benzoyl-D-mannitol[22] (**16**; 2.99 g, 5 mmol) and 2,4,6-trimethylpyridine (1.45 mL, 11 mmol) in dichloromethane (50 mL). After 1 h, the mixture was worked-up as described above. Column chromatography (solvent *D*) of the product gave **16** (1.46 g) and **17** (1.20 g, 27%), as an amorphous powder, $[\alpha]_D$ +2° (*c* 1.2), R_F 0.60 (solvent *C*).

4-O-Acetyl-1,2,5,6-tetra-O-benzoyl-3-O-trityl-D-mannitol (**18**). — To a solution of **17** (1.68 g, 2 mmol) in pyridine (25 mL) were added acetic anhydride (0.45 mL, 5 mmol) and 4-dimethylaminopyridine (122 mg, 1 mmol). The mixture was kept at room temperature for 14 h, treated with methanol (1 mL), and, after 30 min, concentrated. Column chromatography (solvent *D*) of the residue gave **18** (1.66 g, 94%) as a white powder, $[\alpha]_D$ +44° (*c* 1.35), R_F 0.66 (solvent *C*). ^1H-N.m.r. data: δ 7.95–7.08 (m, 35 H, 7 Ph), 5.85 (t, 1 H, $J_{4,5} = J_{3,4}$ = 6 Hz, H-4), 5.68–5.56 (m, 2 H, H-2,5), 4.95 (d, 2 H, *J* 6 Hz, CH_2OBz), 4.47 (d, 2 H, *J* 6 Hz, CH_2OBz), 4.06 (dd, 1 H, $J_{2,3}$ 3 Hz, H-3), 1.74 (s, 3 H, AcO).

Synthesis of disaccharide derivatives. — In one limb of a tuning-fork-shaped tube (⅄) was placed a solution of a trityl ether (0.55 mmol) and the 1,2-*O*-cyanoalkylidene derivative (0.50 mmol) in nitromethane (2 mL), a solution of triphenylmethylium perchlorate (0.05 mmol) in nitromethane (0.2 mL) was placed in the

other limb, and the solutions were lyophilised. Benzene (2 mL) was twice distilled into, and lyophilised from, the limb with reagents followed by drying for several hours. Dichloromethane (2 mL) was distilled into both limbs of the tube, and the solutions were mixed, and left overnight at room temperature in the dark (lyophilisation and drying of the reactants, as well as distillation from CaH_2 of benzene and dichloromethane, was carried out at 4×10^{-3} mmHg). The bright-yellow reaction mixture was treated with 3:1 pyridine–water (1 mL), and the decolourised solution was diluted with chloroform (50 mL), washed with water (3 × 30 mL), and concentrated. The residue was subjected to column chromatography. The following compounds were obtained thus.

Methyl 2,3-O-isopropylidene-4-O-(2,3,5-tri-O-acetyl-α-L-arabinofuranosyl)-α-L-rhamnopyranoside (**19**). — (*a*) Prepared from **4** and **11, 19** (96%) was a syrup, $[\alpha]_D$ −75.5° (*c* 1), R_F 0.39 (solvent *A*).

(*b*) Prepared from **5** and **11, 19** (91%) was a syrup, $[\alpha]_D$ −78° (*c* 1), R_F 0.39; lit.[21] $[\alpha]_D$ −81.6° (chloroform).

Methyl 2,3-O-isopropylidene-4-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-α-L-rhamnopyranoside (**20**). — Prepared from **10** and **11, 20** (82%) had m.p. 112–114° (from toluene–hexane), $[\alpha]_D$ −20° (*c* 1.75), R_F 0.67 (solvent *A*); lit.[21] syrup, $[\alpha]_D$ −18.8° (chloroform).

Anal. Calc. for $C_{36}H_{38}O_{12}$: C, 65.25; H, 5.78. Found: C, 65.15; H, 5.70.

The product obtained after concentration of the mother liquor had $[\alpha]_D$ −18.5° (*c* 1.4) and R_F 0.67.

1,2,3,4-Tetra-O-acetyl-6-O-(2,3,5-tri-O-acetyl-α-L-arabinofuranosyl)-β-D-glucopyranose (**21**). — (*a*) Prepared from **4** and **12, 21** (96%) had m.p. 106.5–108.5° (from ether–pentane), $[\alpha]_D$ −26.5° (*c* 1.5), R_F 0.35 (solvent *A*).

(*b*) Prepared from **5** and **12, 21** (90%) had m.p. 106–108°, $[\alpha]_D$ −26.5° (*c* 1.5), R_F 0.35; lit.[21] m.p. 107–109°, $[\alpha]_D$ −21.0° (chloroform).

The product obtained after concentration of the mother liquor had $[\alpha]_D$ −26.2° (*c* 1.7), R_F 0.35.

1,2,3,4-Tetra-O-acetyl-6-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-β-D-glucopyranose (**22**). — Prepared from **10** and **12, 22** (95%) was a syrup, $[\alpha]_D$ +22° (*c* 1.4), R_F 0.45 (solvent *A*); lit.[21] m.p. 73–75°, $[\alpha]_D$ +21.0° (chloroform).

Methyl 2,3-di-O-acetyl-5-O-(2,3,5-tri-O-acetyl-α-L-arabinofuranosyl)-α-L-arabinofuranoside (**23**). — (*a*) Prepared from **4** and **13, 23** (81%) was a syrup, $[\alpha]_D$ −86° (*c* 1), R_F 0.24 (solvent *A*).

(*b*) Prepared from **5** and **13, 23** (83%) was a syrup, $[\alpha]_D$ −83° (*c* 1.5), R_F 0.24; lit.[21] $[\alpha]_D$ −83.0° (chloroform).

Methyl 2,3-di-O-acetyl-5-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-α-L-arabinofuranoside (**24**). — Prepared from **10** and **13, 24** (91%) was a syrup, $[\alpha]_D$ −24° (*c* 1.3), R_F 0.56 (solvent *A*); lit.[21] $[\alpha]_D$ −20.6° (chloroform).

Methyl 2,3-O-isopropylidene-4-O-(2,3,5,6-tetra-O-acetyl-β-D-galactofuranosyl)-α-L-rhamnopyranoside (**25**). — Prepared from **6** and **11, 25** (97%) was a syrup, $[\alpha]_D$ −60.5° (*c* 2.4), R_F 0.30 (solvent *A*).

Methyl 2,3-O-isopropylidene-4-O-(2,3,5,6-tetra-O-acetyl-β-D-glucofuranosyl)-α-L-rhamnopyranoside (**26**). — Prepared from **8** and **11, 26** (89%) was a syrup, $[\alpha]_D$ −57° (*c* 1.8), R_F 0.42 (solvent *A*).

Anal. Calc. for $C_{24}H_{36}O_{14}$: C, 52.54; H, 6.63. Found: C, 52.60; H, 6.61.

Methyl 3,5-di-O-acetyl-2-O-(2,3,5-tri-O-acetyl-α-L-arabinofuranosyl)-α-L-arabinofuranoside (**27**). — Prepared from **5** and **14, 27** (79%) was a syrup, $[\alpha]_D$ −102° (*c* 1.5), R_F 0.36 (solvent *A*).

Methyl 3,5-di-O-acetyl-2-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-α-L-arabinofuranoside (**28**). — Prepared from **10** and **14, 28** (81%) was a syrup, $[\alpha]_D$ −34° (*c* 0.9), R_F 0.64 (solvent *A*).

Methyl 2,5-di-O-acetyl-3-O-(2,3,5-tri-O-acetyl-α-L-arabinofuranosyl)-α-L-arabinofuranoside (**29**). — Prepared from **5** and **15, 29** (71%) had m.p. 83.5–85° (from toluene–hexane), $[\alpha]_D$ −132° (*c* 1.2), R_F 0.36 (solvent *A*).

Anal. Calc. for $C_{21}H_{30}O_{14}$: C, 49.80; H, 5.97. Found: C, 50.16; H, 5.95.

The product obtained after concentration of the mother liquor had $[\alpha]_D$ −126° (*c* 2.2), R_F 0.36.

Methyl 2,5-di-O-acetyl-3-O-(2,3,5-tri-O-benzoyl-α-L-arabinofuranosyl)-α-L-arabinofuranoside (**30**). — Prepared from **10** and **15, 30** (85%) was a syrup, $[\alpha]_D$ −45° (*c* 1.6), R_F 0.64 (solvent *A*).

4-O-Acetyl-1,2,5,6-tetra-O-benzoyl-3-O-(2,3,5,6-tetra-O-acetyl-β-D-galactofuranosyl)-D-mannitol (**31**). — (*a*) Prepared from **6** and **18, 31** (89%) was a white powder, $[\alpha]_D$ −7° (*c* 1.6), R_F 0.39 (solvent *A*).

Anal. Calc. for $C_{50}H_{50}O_{20}$: C, 61.84; H, 5.20. Found: C, 62.17; H, 4.92.

(*b*) Prepared from **7** and **18, 31** (93%) had $[\alpha]_D$ −5° (*c* 0.7), R_F 0.39 (solvent *A*). ^{1}H-N.m.r. data: δ 8.04–7.91 and 7.59–7.30 (2 m, 20 H, 4 Ph), 5.84 (dd, 1 H, $J_{3,4}$ 2.8, $J_{4,5}$ 7.5 Hz, H-4), 5.72 (ddd, 1 H, $J_{5,6a}$ 2.5, $J_{5,6b}$ 5.0 Hz, H-5), 5.62 (m, 1 H, H-2), 5.39 (d, 1 H, $J_{1',2'}$ 0.7 Hz, H-1'), 5.29 (ddd, 1 H, $J_{4',5'}$ 5.0, $J_{5',6'a}$ 3.9, $J_{5',6'b}$ 7.0 Hz, H-5'), 5.20 (dd, 1 H, $J_{2',3'}$ 1.7 Hz, H-2'), 5.07 (dd, 1 H, $J_{3',4'}$ 4.2 Hz, H-3'), 4.97 (dd, 1 H, $J_{1a,1b}$ 12.5, $J_{1a,2}$ 2.8 Hz, H-1a), 4.90 (dd, 1 H, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.66 (dd, 1 H, $J_{1b,2}$ 5.9 Hz, H-1b), 4.56–4.39 (m, 2 H, H-3, H-6b), 4.41 (dd, 1 H, H-4'), 4.25 (dd, 1 H, $J_{6'a,6'b}$ 12.0 Hz, H-6'a), 4.03 (dd, 1 H, H-6'b), 2.14, 2.13, 2.05, 2.01, 1.89 (5 s, each 3 H, 5 AcO).

3-O-β-D-Galactofuranosyl-D-mannitol (**32**). — To a solution of **31** (295 mg, 0.3 mmol) in chloroform (2 mL) was added methanolic 0.05M sodium methoxide (10 mL); after 3 h, the mixture was neutralised with QU-2(pyridinium) resin and then concentrated. A solution of the residue in water (5 mL) was washed with hexane (2 × 5 mL) and concentrated, and the residue was crystallised from ethanol–acetone–ether at 0° to give **32** (53 mg, 51%), m.p. 157–160°, $[\alpha]_D$ −70° (*c* 1.95, water); lit.[23] m.p. 158.5–159°, $[\alpha]_D$ −60° (water); lit.[29] m.p. 161–163°, $[\alpha]_D$ −64° (water).

REFERENCES

1 N. K. KOCHETKOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1982) 1543–1572.
2 V. I. BETANELI, M. V. OVCHINNIKOV, L. V. BACKINOWSKY, AND N. K. KOCHETKOV, *Carbohydr. Res.*, 68 (1979) c11–c13.
3 L. V. BACKINOWSKY, N. E. NIFANT'EV, V. I. BETANELI, M. I. STRUCHKOVA, AND N. K. KOCHETKOV, *Bioorg. Khim.*, 9 (1983) 74–78.
4 N. K. KOCHETKOV, V. I. BETANELI, M. V. OVCHINNIKOV, AND L. V. BACKINOWSKY, *Tetrahedron*, 37 (1981) Suppl. 9, 149–156.
5 B. COXON AND H. G. FLETCHER, JR., *J. Am. Chem. Soc.*, 85 (1963) 2637–2642.
6 I. V. OBRUCHNIKOV AND N. K. KOCHETKOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1977) 2571–2573.
7 V. I. BETANELI, M. M. LITVAK, L. V. BACKINOWSKY, AND N. K. KOCHETKOV, *Carbohydr. Res.*, 94 (1981) c1–c4.
8 F. G. DE LAS HERAS AND P. FERNÁNDEZ-RESA, *J. Chem. Soc., Perkin Trans. 1*, (1982) 903–907; K UTIMOTO AND T. HORIIE, *Tetrahedron Lett.*, 23 (1982) 237–238.
9 R. D. GUTHRIE AND S. C. SMITH, *Chem. Ind. (London)*, (1968) 547–548.
10 B. L KAM, J.-L. BARASCUT, AND J.-L. IMBACH, *Carbohydr. Res.*, 69 (1979) 135–142.
11 R. K. NESS, H. G. FLETCHER, JR., AND C. S. HUDSON, *J. Am. Chem. Soc.*, 73 (1951) 3742–3744.
12 R. E. GRAMERA, A. PARK, AND R. L. WHISTLER, *J Org. Chem.*, 28 (1963) 3230–3231.
13 R. L. WHISTLER AND L. U. DONER, *Carbohydr. Res.*, 15 (1970) 391–395.
14 J. E. CHRISTENSEN AND L. GOODMAN, *Carbohydr. Res.*, 7 (1968) 510–512.
15 N. B. D'ACCORSO, I. M. E. THIEL, AND M. SCHULLER, *Carbohydr. Res.*, 124 (1983) 177–184.
16 R. J. ABRAHAM, L. D. HALL, L. HOUGH, AND K. A. LAUCHLAN, *J. Chem. Soc.*, (1962) 3699–3705.
17 L. D. HALL, S. A. BLACK, K. N. SLESSOR, AND A. S. TRACEY, *Can. J. Chem.*, 50 (1972) 1912–1924.
18 L. G. VORONTSOVA, M. O DECKAPRILEVICH, O. S. CHIZHOV, L. V. BACKINOWSKY, V. I. BETANELI, AND M. V. OVCHINNIKOV, *Izv Akad. Nauk SSSR, Ser. Khim.*, (1980) 2311–2319.
19 V. I. BETANELI, M. V. OVCHINNIKOV, L. V. BACKINOWSKY, AND N. K. KOCHETKOV, *Carbohydr. Res.*, 76 (1979) 252–256.
20 R. L. WHISTLER, L. U. DONER, AND M. KOSIK, *Methods Carbohydr. Chem* , 6 (1972) 411–412.
21 N. F. BALAN, L. V. BACKINOWSKY, AND N. K. KOCHETKOV, *Bioorg. Khim.*, 6 (1970) 1657–1666.
22 E. FISCHER, *Ber.*, 48 (1915) 266–275.
23 N. K. KOCHETKOV, A. YA. KHORLIN, AND A. F. BOCHKOV, *Tetrahedron*, 23 (1967) 693–707.
24 K. BOCK AND C. PEDERSEN, *Carbohydr. Res.*, 29 (1973) 331–338.
25 R. K. NESS AND H. G. FLETCHER, JR., *J. Am. Chem Soc* , 80 (1958) 2007–2010.
26 J. D. STEVENS AND H. G. FLETCHER, JR., *J. Org. Chem.*, 33 (1968) 1799–1803.
27 L. V BACKINOWSKY, N. F. BALAN, A. S. SHASHKOV, AND N. K. KOCHETKOV, *Carbohydr. Res.*, 84 (1980) 225–235.
28 H. J. DAUBEN, JR., L. R. HONNEN, AND K. M. HARMON, *J. Org. Chem.*, 25 (1960) 1442–1445.
29 B. LINDBERG, B.-G. SILVANDER, AND C. A. WACHTMEISTER, *Acta Chem. Scand* , 18 (1964) 213–216.