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REACTION OF 3-HETERO-1,5-DIALDEHYDES WITH *tert*-BUTYL CYANOACETATE*

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ABSTRACT

The reaction of thiodiglycolaldehyde and diglycolaldehyde with *tert*-butyl cyanoacetate yields derivatives of tetrahydrothiopyran and tetrahydropyran, respectively. Similar reactions of diglycolaldehyde derivatives having a furan nucleus at the α-position yield D-*xylo* (major) and L-*arabino* (minor) *C*-pyranosyl derivatives. Starting from α-(*S*)-methoxy-α′-(*R*)-hydroxymethyldiglycolaldehyde, D-*gluco* and D-*manno* glycosides were obtained, the relative proportions of which depended on the time of reaction. In addition to the 1:1 addition products, minor products corresponding to 1:2 (dialdehyde:active methylene compound) addition were isolated.

INTRODUCTION

The present work is part of a programme on the synthesis of 3-deoxy-*C*-glycosyl derivatives and 3-deoxyglycosides branched at C-3 by the reaction of 3-hetero-1,5-dialdehydes with active methylene compounds[2–4].

We have reported[1,5–7] on the reaction of thiodiglycolaldehyde (**1**), diglycolaldehyde (**2**), α-(*S*)-(3-ethoxycarbonyl-2-methylfur-5-yl)diglycolaldehyde (**3**), and α-(*S*)-(3-acetyl-2-methylfur-5-yl)diglycolaldehyde (**4**) with 2,4-pentanedione, ethyl acetoacetate, ethyl cyanoacetate, malononitrile, and cyanoacetamide, and we now report on similar reactions using *tert*-butyl cyanoacetate.

Three types of dialdehyde were used: (*a*) thiodiglycolaldehyde (**1**) and diglycolaldehyde (**2**), which have no substituents in the α- and α′-positions; (*b*) hydrates of dialdehydes having furan substituents at the α-position, namely, α-(*S*)-(3-ethoxycarbonyl-2-methylfur-5-yl)diglycolaldehyde (**3**) and α-(*S*)-(3-acetyl-2-methylfur-5-yl)diglycolaldehyde (**4**) that can lead to *C*-pyranosyl derivatives branched at C-3; and (*c*) dialdehydes substituted at the α- and α′-positions, such as α-(*S*)-methoxy-α′-(*R*)-hydroxymethyldiglycolaldehyde (**5**), that lead to pyranosides branched at C-3.

*Derivatives of 3-Hetero-1,5-dialdehydes, Part XVI. For Part XV, see ref. 1.

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RESULTS AND DISCUSSION

The reactions were carried out in aqueous 1,4-dioxane at room temperature using piperidine (1%) as catalyst. The molar ratios of dialdehyde and active methylene compound were 1:1 or 1:2. The products from **1–5** were isolated by column chromatography. Dialdehydes of the type **1–5** exist in equilibrium with cyclic hydrated forms[9,11–13] but, for simplicity, they are depicted as dialdehydes.

The reaction of **1** with *tert*-butyl cyanoacetate gave the thiopyran derivative **6** as the only isolated product, but **2** gave the pyran derivatives **7** (major) and **8** (minor)(mixture of stereoisomers).

Likewise, using a ~1:1 ratio of starting materials, the hydrates of **3** and **4** gave, as the major and minor isolated products, **9** and **10**, and **11** and **12**, respectively, corresponding to 1:1 addition. A small amount of **13** was also isolated from **3**. When 2 mol of active methylene compound was used together with a longer reaction time, the 1:1 addition compounds from **3** were the major products and the pyran derivatives **13** and **14**, respectively, were the minor products, both corresponding to 1:2 addition.

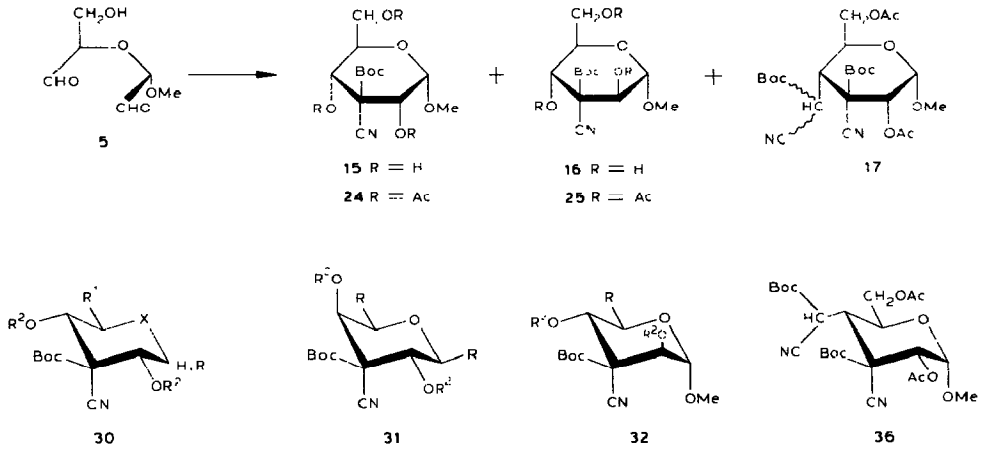
With **5** and a short reaction time, the major product was a ~1:1 mixture of the isomers **15** and **16**, and the minor product of 1:2 addition was isolated as the diacetate **17**. The same reagents and longer reaction time gave **15** and **16** in the ratio ~4:1.

The structures of **6, 7, 9–12, 15**, and **16** were established on the basis of elemental analyses and spectroscopic data, together with those of the corresponding acetates **18–25** and benzoates **26–29**. The configurations at C-2 and C-4 were deduced from the values of $J_{1,2}$, $J_{4,5a}$, and $J_{4,5e}$ in the ^{1}H-n.m.r. spectra, leading to the generalised structures **30–32**. The n.m.r. spectra of the hydroxy compounds **7, 9, 10**, and **15** were poorly resolved, but a study of their acetylated and benzoylated derivatives, discussed below, led to the structure **30**.

Compounds **6, 9, 10, 18–23**, and **26–29** showed $J_{1,2}$ values of 8.0–10.5 Hz, indicating H-1,2 to be *trans*-diaxial in $^4C_1$(D) conformations. The same can be said for the configurations at C-4 and C-5 in **6, 18, 19–21**, and **24–29**, which showed $J_{4,5a}$ values of 8.0–11.0 Hz. On the other hand, **15** and **24** had $J_{1,2}$ values of 3.7 and 3.5 Hz, respectively, in accordance with the equatorial,axial disposition of H-1,2. However, the isomer **25** had a $J_{1,2}$ value of 1.7 Hz in agreement with the equatorial,equatorial disposition of H-1,2 in **32**. For the minor products **22** and **23**, the signal for H-4 was a broad singlet reflecting a synclinal relationship with H-5*a*,5*e* in agreement with the supposed configuration and conformation **31**.

The configuration at C-3 in **6–9, 10–12, 16**, and **18–29** was assigned tentatively on the basis of the expected higher stability of an equatorial *tert*-butoxycarbonyl group and an axial cyano group in the depicted conformations **30–32**, which accords with the chemical shifts of the signals for the CMe_3 protons. These appeared at δ ~1.5 for compounds **6, 7, 9, 10**, and **15**, with unprotected hydroxyl groups, or their acetates **18–25**, but moved to δ 1.25–1.32 for the benzoates **26–29**. This finding may

1 X = S
2 X = O
3 R = OEt
4 R = Me
6 X = S, R = H
7 X = O, R = H
18 X = S, R = Ac
19 X = O, R = Ac
26 X = S, R = Bz
27 X = O, R = Bz
8 X = O, R = H
33 X = O, R = Ac
9 R¹ = OEt, R² = H
10 R¹ = Me, R² = H
20 R¹ = OEt, R² = Ac
21 R¹ = Me, R² = Ac
28 R¹ = OEt, R² = Bz
29 R¹ = Me, R² = Bz
11 R¹ = OEt, R² = H
12 R¹ = Me, R² = H
22 R¹ = OEt, R² = Ac
23 R¹ = Me, R² = Ac
13 R = H, R¹ = OEt
14 R = H, R¹ = Me
34 R = Ac, R¹ = OEt
35 R = Ac, R¹ = Me



be attributed to the deshielding effect of the benzoyl groups if the corresponding groups assume equatorial, equatorial positions.

The structures of the minor products **8, 13**, and **14** were also established on the basis of elemental analysis and spectroscopic data. They were formed as mixtures of stereoisomers, as deduced from the ^{1}H- and ^{13}C-n.m.r. spectra of the acetylated derivatives **33–35**. Product **33** showed three signals at δ 2.1, 2.07, and 2.05 (3 s, each 3 H, 3 Ac) corresponding to three stereoisomers. Crystallisation of the mixture from hexane gave a product that showed only the signals at δ 2.1 and 2.07. The products **34** and **35** were mixtures of two stereoisomers with the signals of H-1,2 appearing as doublets with $J_{1,2}$ ~10.0 Hz (*trans*-diaxial disposition in the $^4C_1$ conformation). The ^{13}C-n.m.r. data confirmed this observation. The signals for C-2,3,4, NC-*C*H-Boc, and *C*Me$_3$ were duplicated, but the diacetate **17**, prepared from α-(*S*)-methoxy-α'-(*R*)-hydroxymethyldiglycolaldehyde (**5**) was a single isomer. The $J_{1,2}$ value of 3.5 Hz accorded with an equatorial,axial disposition of H-1,2, whereas the $J_{4,5}$ value of ~10 Hz indicated H-4,5 to be axial,axial. All these values accord with the $^4C_1$(D) conformation **36**. The configuration of C-3 is assumed to be as for **6, 9, 10–12, 16**, and **18–29**, *i.e.*, axial cyano and equatorial *tert*-butoxycarbonyl.

The i.r. band at ~2250 cm^{-1} for cyano[16] was not observed for **8, 9, 13, 16–29**, and **33–35**, and was weak for **6, 7, 10, 11**, and **15**, as found[1,17] for cyano groups near to oxygenated functions.

EXPERIMENTAL

The general methods have been described[14]. N.m.r. spectra (^{1}H, 80 and 200 MHz; ^{13}C, 20 MHz) were obtained with Bruker WP-80-SY and WP-200 spectrometers. Thiodiglycolaldehyde (**1**) was used in the form of its hydrate *cis*-2,6-dihydroxy-1,4-oxathiane and was obtained from thiodiglycolaldehyde bis(dimethyl acetal)[11] (90%) or from thiodiglycolaldehyde bis(diethyl acetal)[11] (>90%).

Elemental analyses could not be obtained for syrupy products. Their homogeneity was established by chromatography, and they were characterised by n.m.r. spectroscopy.

Reaction of tert-*butyl cyanoacetate*[15] *with* **1–5**. — *tert*-Butyl cyanoacetate containing 1% of piperidine was added to a solution of the dialdehyde (**1–5**) in aqueous 1,4-dioxane (2:1). The mixture was stored at room temperature and then concentrated, water (15 mL) was added, and the mixture was extracted with ethyl acetate (4 × 40 mL). The combined extracts were dried, filtered, and concentrated to give the crude product.

The following amounts and conditions were used:

Starting compound (g)	tert-*Butyl cyanoacetate (g)*	*1,4-Dioxane–water (2:1, mL)*	*Time (h)*	*Products (g, %)*
1 (1.0)	1.1	15	16	**6** (1.34, 70.3)
2[a]	1.1	15	16	**7** (1.03, 58.5)
				8 (0.45, 17.0)
3 (2.0)	1.1	21	4	**9** (1.75, 60.2)
				11 (0.16, 5.5)
				13 (0.18, 4.7)
3 (1.5)	1.55	15	66	**9** + **11** (1.0, 45.8)
				13 (0.62, 21.6)
4 (1.0)	0.6	15	6	**10** + **12** (0.9, 59.6)
4 (1.9)	2.2	21	30	**10** + **12** (1.3, 45.3)
				14 (0.65, 17.0)
5[b]	2.11	15	15	**15** + **16** (2.54, 56.8)
				17 (0.58, 7.5)
5[b]	2.11	15	96	**15** + **16** (1.9, 42.5)

[a]Diglycolaldehyde (**2**) was prepared in the polymeric state from its bis(dimethyl acetal)[8] (1.42 g, 7.32 mmol) or bis(di-isopropyl acetal)[9] (2.24 g, 7.32 mmol). [b]Compound **5** was prepared from methyl α-D-glucopyranoside[10] (2.91 g, 15 mmol).

(*a*) *With thiodiglycolaldehyde*[11] (**1**). Column chromatography (2:1 ether–hexane) of the crude product gave *r*-4-*tert*-butoxycarbonyl-4-cyano-*t*-3,*t*-5-dihydroxytetrahydrothiopyran (**6**), m.p. 159–160° (from hexane–ether); ν_{max}^{KBr} 3500–3400, 2260, 1745, 1368, 1280, 1260, 1150, 1060, 1038, 988, 904, 865, 820, and 744 cm^{-1}. ^{1}H-N.m.r. data [$(CD_3)_2SO$, 80 MHz]: δ 6.15 (d, 2 H, *J* 5.0 Hz, exchangeable with D_2O, 2 OH), 3.87 (m, 2 H, H-3,5; dd, *J* 8.0 and 6.0 Hz, after isotopic change), 2.57 (m, 4 H, H-2,6,2′,6′), and 1.45 (s, 9 H, Me_3C) (Found: C, 51.14; H, 6.72; N, 5.31. $C_{11}H_{17}NO_4S$ calc.: C, 50.95; H, 6.61; N, 5.40%).

(*b*) *With diglycolaldehyde*[8,9] (**2**). Column chromatography (2:1 ether–hexane) of the crude product gave, first, 4-*tert*-butoxycarbonyl-5-(1-*tert*-butoxycarbonyl-1-cyanomethyl)-4-cyano-3-hydroxytetrahydropyran (**8**), isolated as a syrup; $\nu_{max}^{CCl_4}$ 3450, 1750, 1367, 1275, 1255, 1150, and 895 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$, 80 MHz): δ 4.30–3.80 (m, 4 H, one exchangeable with D_2O, H-2,3,6 and OH), 3.75–2.75 (m, 4 H, H-5,2′,6′ and NC-CH-Boc), and 1.62–1.40 (5 s, 18 H, 2 Me_3C).

Eluted second was *r*-4-*tert*-butoxycarbonyl-4-cyano-*t*-3,*t*-5-dihydroxytetrahydropyran (**7**), m.p. 132–133° (from hexane–ether); ν_{max}^{KBr} 3470, 3410, 2255, 1745,

1370, 1280, 1130, 1112, 1092, 1060, 934, and 820 cm^{-1}. ^{1}H-N.m.r. data [$(CD_3)_2SO$, 80 MHz]: δ 6.0 (d, 2 H, *J* 5.0 Hz, exchangeable with D_2O, 2 OH), 3.90–3.60 (m, 4 H, H-2*e*,3,5,6*e*), 3.15 (m, 2 H, H-2*a*,6*a*), and 1.45 (s, 9 H, Me_3C) (Found: C, 54.55; H, 7.24; N, 5.73. $C_{11}H_{17}NO_5$ calc.: C, 54.31; H, 7.04; N, 5.75%).

(*c*) *With* α-(S)-*(3-ethoxycarbonyl-2-methylfur-5-yl)diglycolaldehyde*[12] (**3**). Column chromatography (2:1 hexane–ether) of the crude product (4-h reaction) gave, first, (2*R*,3*R*,4*R*)-4-*tert*-butoxycarbonyl-5-(1-*tert*-butoxycarbonyl-1-cyanomethyl)-4-cyano-2-(3-ethoxycarbonyl-2-methylfur-5-yl)-3-hydroxytetrahydropyran (**13**), m.p. 68–69° (from hexane–ether); $[\alpha]_{4360}^{20}$ −2.3° (*c* 1, chloroform); ν_{max}^{KBr} 3580–3220, 1765, 1730, 1635, 1600, 1380, 1285, 1267, 1240, 1160, 1098, 835, and 780 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$, 80 MHz): δ 6.75 (bs, 1 H, furan H), 4.51–3.75 (m, 6 H, H-2,3,6,6′ and CH_3CH_2O), 3.50 (m, 1 H, NC-CH-Boc), 3.0 (m, 1 H, H-5), 2.70 (bs, 1 H, exchangeable with D_2O, OH), 2.55 (s, 3 H, furan Me), 1.55 and 1.50 (2 s, 18 H, 2 Me_3C), and 1.32 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O) (Found: C, 60.24; H, 6.42; N, 5.17. $C_{26}H_{34}N_2O_9$ calc.: C, 60.22; H, 6.61; N, 5.40%).

Eluted second was 5-(3-*tert*-butoxycarbonyl-3-*C*-cyano-3-deoxy-α-L-*arabino*-pentopyranosyl)-3-ethoxycarbonyl-2-methylfuran (**11**), isolated as a syrup, $[\alpha]_D^{28}$ +16.5° (*c* 0.75, chloroform); $\nu_{max}^{CCl_4}$ 3540–3350, 2230, 1738, 1722, 1620, 1587, 1367, 1260, 1222, 1150, 1120, 1080, and 836 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$, 80 MHz): δ 6.75 (s, 1 H, furan H), 4.6–4.0 (m, 7 H, H-1,2,4,5,5′ and CH_3CH_2O), 2.8 (bs, 1 H, exchangeable with D_2O, OH), 2.57 (s, 3 H, furan Me), 1.55 (s, 10 H, one exchangeable with D_2O, Me_3C, and OH), and 1.32 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O).

Eluted third was 5-(3-*tert*-butoxycarbonyl-3-*C*-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-3-ethoxycarbonyl-2-methylfuran (**9**), m.p. 117–118° (from ether–hexane), $[\alpha]_D^{20}$ −18° (*c* 1, chloroform); ν_{max}^{KBr} 3600–3250, 1740, 1690, 1620, 1580, 1370, 1290, 1238, 1160, 1065, 945, 832, and 775 cm^{-1}. N.m.r. data: ^{1}H ($CDCl_3$, 80 Hz), δ 6.75 (s, 1 H, furan H), 4.45 (d, 1 H, *J* 10.0 Hz, H-1), 4.30 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 4.25–4.00 (m, 3 H, H-2,4,5*e*), 3.70 (m, 1 H, H-6*a*), 2.60 (bs, 2 H, exchangeable with D_2O, 2 OH), 2.55 (s, 3 H, furan Me), 1.55 (s, 9 H, Me_3C), and 1.32 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O); ^{13}C [$(CD_3)_2CO$], δ 166.17, 163.59 (COO), 159.42 (furan C-2), 149.52 (furan C-5), 115.60 (CN), 114.62 (furan C-3), 111.19 (furan C-4), 84.00 (CMe_3), 74.01, 70.86, 69.47 (C-1,2,4), 68.72 (C-5), 62.88 (C-3), 60.21 (CH_2CH_3), 27.64 (Me_3C), 14.19 and 13.32 (furan Me, CH_3CH_2) (Found: C, 57.79; H, 6.34; N, 3.46. $C_{19}H_{25}NO_8$ calc.: C, 57.71; H, 6.37; N, 3.54%).

The reaction of the **3** with an excess of *tert*-butyl cyanoacetate at room temperature (66 h) gave **13**, **9** + **11**, and **11** (minor isomer).

(*d*) *With* α-(S)-*(3-acetyl-2-methylfur-5-yl)diglycolaldehyde*[13] (**4**). Column chromatography (1:2 hexane–ether) of the crude product (6-h reaction) gave a mixture of 3-acetyl-5-(3-*tert*-butoxycarbonyl-3-*C*-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-2-methylfuran (**10**) and 3-acetyl-5-(3-*tert*-butoxycarbonyl-3-*C*-cyano-3-deoxy-α-L-*arabino*-pentopyranosyl)-2-methylfuran (**12**). Compound **10** had m.p. 153–155° (from ether), $[\alpha]_D^{20}$ −20° (*c* 1.1, chloroform); ν_{max}^{KBr} 3550–3270, 2230, 1750, 1680, 1615, 1575, 1375, 1290, 1235, 1160, 1080, 930, and 835 cm^{-1} N.m.r. data: ^{1}H

($CDCl_3$, 80 MHz), δ 6.72 (s, 1 H, furan H), 4.45 (d, 1 H, *J* 10.0 Hz, H-1), 4.35–4.00 (m, 3 H, H-2,4,5*e*), 3.65 (pseudo-t, 1 H, *J* 10.5 Hz, H-5*a*), 2.67 (d, 1 H, *J* 5.0 Hz, exchangeable with D_2O, OH), 2.60 (d, 1 H, *J* 6.0 Hz, exchangeable with D_2O, OH), 2.57 (s, 3 H, furan Me), 2.37 (s, 3 H, furan Ac), and 1.60 (s, 9 H, Me_3C); ^{13}C [$(CD_3)_2CO$], δ 193.65 (COMe), 166.21 (COO), 158.35 (furan C-2), 149.23 (furan C-5), 122.52 (furan C-3), 115.65 (CN), 111.40 (furan C-4), 84.08 (CMe_3), 74.08 (C-1), 70.84, 69.51 (C-2,4), 68.75 (C-5), 62.87 (C-3), 28.77 (*Me*CO-furan), 27.68 (Me_3C), and 13.88 (furan Me) (Found: C, 59.39; H, 6.30; N, 3.66. $C_{18}H_{23}NO_7$ calc.: C, 59.17; H, 6.35; N, 3.83%).

The reaction of **4** with an excess of *tert*-butyl cyanoacetate at room temperature (30 h) and column chromatography (ether–hexane 1:1→2:1) of the crude product gave, first, (2*R*,3*R*,4*R*)-2-(3-acetyl-2-methylfur-5-yl)-4-*tert*-butoxycarbonyl-5-(1-*tert*-butoxycarbonyl-1-cyanomethyl)-4-cyano-3-hydroxytetrahydropyran (**14**, 17%), m.p. 134–137° (from hexane–ether), $[\alpha]_{4360}^{30}$ −9° (*c* 1, chloroform); ν_{max}^{KBr} 3460, 3270, 2230, 1762, 1750, 1700, 1690, 1628, 1580, 1382, 1320–1290, 1270, 1162, 1100, 955, and 830 cm^{-1}. ^1H-N.m.r. data ($CDCl_3$, 80 MHz): δ 6.67 (bs, 1 H, furan H), 4.55–3.90 (m, 3 H, H-2,3,6*e*), 3.76–3.25 (m, 2 H, H-6*a* and NC-C*H*-Boc), 3.20–2.80 (m, 2 H, one exchangeable with D_2O, H-5 and OH), 2.51 (s, 3 H, furan Me), 2.32 (s, 3 H, furan Ac), 1.55, 1.50, and 1.48 (3 s, 18 H, 2 Me_3C) (Found: C, 61.10; H, 6.36; N, 5.60. $C_{25}H_{32}N_2O_8$ calc.: C, 61.46; H, 6.60; N, 5.73%).

Eluted second was a mixture of **10** and **12**.

(*e*) *With* α-(S)-*methoxy*-α′-(R)-*hydroxymethyldiglycolaldehyde* (**5**). Column chromatography (ether) of the crude product (15-h reaction) gave, first, a product which was treated with acetic anhydride–pyridine (1.4:1, 24 mL). Column chromatography (1:1 hexane–ether) of the crude product gave methyl 2,6-di-*O*-acetyl-3-*tert*-butoxycarbonyl-4-(1-*tert*-butoxycarbonyl-1-cyanomethyl)-3-*C*-cyano-3,4-dideoxy-α-D-*gluco*-hexopyranoside (**17**; 0.58 g, 7.5%), m.p. 140° (from hexane–ether), $[\alpha]_D^{26}$ +40° (*c* 1, chloroform); ν_{max}^{KBr} 1758, 1372, 1272, 1262, 1213, 1147, 1054, 1027, and 820 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H (80 MHz), δ 5.30 (d, 1 H, *J* 3.5 Hz, H-2), 4.96 (d, 1 H, *J* 3.5 Hz, H-1), 4.50–4.15 (m, 3 H, H-5 and CH_2OAc), 3.65 (bs, 1 H, NC-C*H*-Boc), 3.47 (s, 3 H, MeO), 3.10 (d, 1 H, *J* 10.5 Hz, H-4), 2.15, 2.10 (2 s, 6 H, 2 Ac), 1.50 and 1.47 (2 s, 18 H, 2 Me_3C); ^{13}C, δ 170.19, 169.80, 163.85, 162.64 (4 COO), 113.73, 112.97, (2 CN), 95.39 (C-1), 86.82, 86.14 (2 CMe_3), 69.94, 65.04 (C-2,5), 63.05 (CH_2OAc), 55.88 (MeO), 51.47 (C-3), 40.11, 37.6 (NC-*C*H-Boc, *C*-4), 27.61 (Me_3C), and 20.76, 20.43 (2 *Me*-COO) (Found: C, 56.45; H, 6.71; N, 5.48. $C_{24}H_{34}N_2O_{10}$ calc.: C, 56.37; H, 6.87; N, 5.46%).

Eluted second was a 1:1 mixture of methyl 3-*tert*-butoxycarbonyl-3-*C*-cyano-3-deoxy-α-D-*gluco*- (**15**) and -α-D-*manno*-hexopyranoside (**16**). Treatment of the mixture (2.54 g) with acetic anhydride–pyridine (7:5 mL) and column chromatography (1:1 hexane–ether) of the crude product gave a mixture (1.86 g, 51.7%) of methyl 2,4,6-tri-*O*-acetyl-3-*tert*-butoxycarbonyl-3-*C*-cyano-3-deoxy-α-D-*gluco*- (**24**) and -α-D-*manno*-hexopyranoside (**25**). Crystallisation of the mixture from 1:1

hexane–ether gave **24**, m.p. 137°, $[\alpha]_D^{26}$ +93.5° (*c* 1, chloroform); ν_{max}^{KBr} 1775, 1755, 1370, 1220, 1135, 1055, and 1024 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H (200 MHz), δ 5.30 (d, 1 H, *J* 10.0 Hz, H-4), 5.27 (d, 1 H, *J* 3.5 Hz, H-2), 4.97 (d, 1 H, *J* 3.5 Hz, H-1), 4.35 (dd, 1 H, *J* 12.5 and 4.5 Hz, H-6), 4.22 (m, 1 H, H-5), 4.17 (dd, 1 H, *J* 12.5 and 2.2 Hz, H-6'), 3.44 (s, 3 H, MeO), 2.12, 2.00, 2.08 (3 s, 9 H, 3 Ac), and 1.43 (s, 9 H, Me_3C); ^{13}C, δ 170.31, 169.02, 168.3, 162.65 (4 COO), 113.93 (CN), 95.50 (C-1), 85.86 (CMe_3), 69.68, 67.04, 65.51 (C-2,4,5), 61.47 (C-6), 55.71 (MeO), 53.57 (C-3), 27.40 (Me_3C), 20.64 and 20.57 (*Me*COO) (Found: C, 53.00; H, 6.09; N, 3.10. $C_{19}H_{27}NO_{10}$ calc.: C, 53.14; H, 6.33; N, 3.26%).

Column chromatography (2:1 hexane–ether) of the material in the mother liquor gave, first, **24** (0.96 g), m.p. 137°. Eluted second was **25** (0.9 g), isolated as a syrup, $[\alpha]_D^{30}$ +35.5° (*c* 1, chloroform); $\nu_{max}^{CCl_4}$ 1770, 1372, 1254, 1220, 1152, 1140, 1088, 1042, and 907 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H (200 MHz), δ 5.55 (d, 1 H, *J* 10.3 Hz, H-4), 5.41 (d, 1 H, *J* 1.7 Hz, H-2), 4.67 (d, 1 H, *J* 1.7 Hz, H-1), 4.31–4.00 (m, 3 H, H-5,6,6'), 3.42 (s, 3 H, MeO), 2.09 (s, 6 H, 2 Ac), 2.07 (s, 3 H, Ac), and 1.42 (s, 9 H, Me_3C); ^{13}C, δ 170.30, 168.73, 168.41, 161.63 (4 COO), 113.70 (CN), 97.25 (C-1), 85.43 (CMe_3), 70.51, 66.11, 63.98 (C-2,4,5), 62.20 (C-6), 55.21 (MeO), 49.60 (C-3), 27.34 (Me_3C), and 20.52 (*Me*COO).

The reaction of **5** with *tert*-butyl cyanoacetate at room temperature (96 h) and column chromatography (ether) of the crude product gave a mixture of **15** and **16** in the ratio 4:1. Crystallisation of the mixture **15** and **16** from ether gave **15**, m.p. 153°, $[\alpha]_D^{30}$ +122° (*c* 0.5, ethanol); ν_{max}^{KBr} 3540, 3470, 3350, 2215, 1740, 1368, 1275, 1258, 1150, 1105, 1080, 1056, 1044, 1030, 932, 893, 820, and 746 cm^{-1}. N.m.r. data [$(CD_3)_2CO$]: ^1H (80 MHz), δ 5.07 (d, 1 H, *J* 6.0 Hz, exchangeable with D_2O, OH), 4.70 (d, 1 H, *J* 3.7 Hz, H-1), 4.30 (d, 1 H, *J* 9.5 Hz, exchangeable with D_2O, OH), 4.05–3.65 (m, 6 H, one exchangeable with D_2O, H-2,4,5,6,6' and OH), 3.4 (s, 3 H, MeO), and 1.5 (s, 9 H, Me_3C); ^{13}C, δ 166.83 (COO), 116.16 (CN), 98.50 (C-1), 83.36 (CMe_3), 71.17, 70.14 , 69.14 (C-2,4,5), 61.03 (C-6), 59.06 (C-3), 54.92 (MeO), and 27.49 (Me_3C) (Found: C, 51.66; H, 7.22; N, 4.58. $C_{13}H_{21}NO_7$ calc.: C, 51.47; H, 6.97; N, 4.61%).

Acetylation of **6–14**. — Conventional treatment of these compounds with acetic anhydride–pyridine and extraction of the products into chloroform gave the following results:

Starting compound (g)	*Ac_2O–pyridine (mL)*	*Products (g, %)*
6 (0.6)	8:4	**18** (0.7, 88)
7 (0.4)	7:3	**19** (0.43, 79.8)
8 (0.4)	7:3	**33** (0.3, 67.2)
9 (0.25)	5:3	**20** (0.27, 95.6)
10 + **12** (0.6)[a]	6:3	**21** (0.54, 73.1), **23** (0.05, 8.3)
11 (0.065)	4:2	**22** (0.055, 70)
13 (0.83)	8:4	**34** (0.32, 35.6)
14 (0.35)	6:3	**35** (0.36, 94.7)

[a]Was obtained from mother liquor of **10**.

(*a*) t-*3*,t-*5*-*Diacetoxy*-r-*4*-tert-*butoxycarbonyl*-*4*-*cyanotetrahydrothiopyran* (**18**). — Column chromatography (2:1 hexane–ether) of the crude product gave **18**, m.p. 119–120° (from hexane–ether); ν_{max}^{KBr} 1780–1740, 1370, 1220–1200, 1190, 1030, 1010, 960, 920, 910, 890, and 823 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$, 80 MHz): δ 5.32 (dd, 2 H, *J* 9.0 and 6.0 Hz, H-3,5), 2.8 (m, 4 H, H-2*a*,2*e*,6*a*,6*e*), 2.10 (s, 6 H, 2 Ac), and 1.47 (s, 9 H, Me_3C) (Found: C, 52.35; H, 6.20; N, 4.03. $C_{15}H_{21}NO_6S$ calc.: C, 52.46; H, 6.16; N, 4.07%).

(*b*) t-*3*,t-*5*-*Diacetoxy*-r-*4*-tert-*butoxycarbonyl*-*4*-*cyanotetrahydropyran* (**19**). — Column chromatography (1:1 hexane–ether) of the crude product gave **19**, m.p. 106–108° (from hexane); ν_{max}^{KBr} 1760, 1745, 1372, 1227, 1210, 1156, 1130, 1118, 1050, 1047, 890, and 828 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$, 80 MHz): δ 5.40 (dd, 2 H, *J* 10.5 and 4.9 Hz, H-3,5), 4.00 (dd, 2 H, *J* 11.5 and 4.9 Hz, H-2*e*,6*e*), 3.50 (dd, 2 H, *J* 11.5 and 10.5 Hz, H-2*a*,6*a*), 2.12 (s, 6 H, 2 Ac), and 1.5 (s, 9 H, Me_3C) (Found: C, 55.34; H, 7.52; N, 4.33. $C_{15}H_{21}NO_7$ calc.: C, 55.04; H, 7.70; N, 4.27%).

(*c*) *5*-*(2,4-Di*-O-*acetyl*-*3*-tert-*butoxycarbonyl*-*3*-*cyano*-*3*-*deoxy*-*β*-D-xylo-*pentopyranosyl)*-*3*-*ethoxycarbonyl*-*2*-*methylfuran* (**20**). — Column chromatography (2:1 hexane–ether) of the crude product gave **20**, m.p. 107° (from ethanol), $[\alpha]_D^{28}$ −17.5° (*c* 1.6, chloroform); ν_{max}^{KBr} 1770, 1745, 1725, 1623, 1585, 1375, 1297, 1285, 1265, 1225, 1150, 1060, 1045, 955, 826, and 773 cm^{-1}. N.m.r. data ($CDCl_3$): ^{1}H (80 MHz), δ 6.67 (s, 1 H, furan H), 5.56 (d, 1 H, *J* 10.0 Hz, H-2), 5.47 (dd, 1 H, *J* 10.5 and 5.5 Hz, H-4), 4.56 (d, 1 H, *J* 10.0 Hz, H-1), 4.25 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 4.20 (dd, 1 H, *J* 11.5 and 5.5 Hz, H-5*e*), 3.71 (dd, 1 H, *J* 11.5 and 10.5 Hz, H-5*a*), 2.56 (s, 3 H, furan Me), 2.10, 1.97 (2 s, 6 H, 2 Ac), 1.47 (s, 9 H, Me_3C), and 1.34 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O); ^{13}C, δ 168.57, 167.70, 163.38, 162.18 (4 COO), 160.09 (furan C-2), 145.91 (furan C-5), 114.74 (furan C-3), 113.64 (CN), 111.29 (furan C-4), 85.96 (CMe_3), 71.78, 68.42, 68.08 (C-1,2,4), 65.40 (C-5), 60.16 (CH_3CH_2O), 57.97 (C-3), 27.42 (Me_3C), 20.24, 20.07 (2 *Me*COO), 14.27 (CH_3CH_2O), and 13.65 (furan Me) (Found: C, 57.90; H, 6.26; N, 2.84. $C_{23}H_{29}NO_{10}$ calc.: C, 57.61; H, 6.10; N, 2.92%).

(*d*) *3*-*Acetyl*-*5*-*(2,4-di*-O-*acetyl*-*3*-tert-*butoxycarbonyl*-*3*-*cyano*-*3*-*deoxy*-*β*-D-xylo-*pentopyranosyl)*- (**21**) *and 3*-*acetyl*-*5*-*(2,4-di*-O-*acetyl*-*3*-tert-*butoxycarbonyl*-*3*-*cyano*-*3*-*deoxy*-*α*-L-arabino-*pentopyranosyl)*-*2*-*methylfuran* (**23**). — Column chromatography (2:1 hexane–ether) of the crude product gave, first, **21**, m.p. 146–148° (from hexane–ether), $[\alpha]_D^{20}$ −22° (*c* 1, chloroform); ν_{max}^{KBr} 1785, 1766, 1748, 1700, 1623, 1576, 1380, 1290, 1213, 1076, 1054, 1030, 943, and 893 cm^{-1}. N.m.r. data ($CDCl_3$): ^{1}H (80 MHz), δ 6.67 (s, 1 H, furan H), 5.55 (d, 1 H, *J* 10.0 Hz, H-2), 5.50 (dd, 1 H, *J* 11.0 and 5.0 Hz, H-4), 4.57 (d, 1 H, *J* 10.0 Hz, H-1), 4.20 (dd, 1 H, *J* 11.5 and 5.0 Hz, H-5*e*), 3.72 (pseudo-t, 1 H, *J* 11.0 Hz, H-5*a*), 2.57 (s, 3 H, furan Me), 2.37 (s, 3 H, furan Ac), 2.12, 1.97 (2 s, 6 H, 2 Ac), and 1.47 (s, 9 H, Me_3C); ^{13}C, δ 193.40, 168.58, 167.77, 162.24 (CO and 3 COO), 159.32 (furan C-2), 146.15 (furan C-5), 122.04 (furan C-3), 113.65 (CN), 110.86 (furan C-4), 86.05 (CMe_3), 71.81, 68.51, 68.10 (C-1,2,4), 65.46 (C-5), 58.02 (C-3), 29.01 (furan Ac), 27.49 (Me_3C), 20.28, 20.13 (2 *Me*COO), and 14.27 (furan Me) (Found: C, 59.18; H, 5.95; N, 2.99. $C_{22}H_{27}NO_9$ calc.: C, 58.79; H, 6.00; N, 3.12%).

Eluted second was **23**, m.p. 71–72°, $[\alpha]_D^{26}$ +7°, $[\alpha]_{4360}^{26}$ +14.5° (*c* 1, chloroform); ν_{max}^{KBr} 1773, 1692, 1620, 1580, 1378, 1215, 1050, 942, 894, and 830 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$):δ 6.70 (s, 1 H, furan H), 5.82 (d, 1 H, *J* 10.0 Hz, H-2), 5.50 (bs, 1 H, H-4), 4.50 (d, 1 H, *J* 10.0 Hz, H-1), 4.12 (m, 2 H, H-5*a*,5*e*), 2.60 (s, 3 H, furan Me), 2.37 (s, 3 H, furan Ac), 2.19, 1.97 (2 s, 6 H, 2 Ac), and 1.49 (s, 9 H, Me_3C) (Found: C, 58.83; H, 5.78; N, 2.97. $C_{22}H_{27}NO_9$ calc.: C, 58.79; H, 6.06; N, 3.12%).

(*e*) *5-(2,4-Di-*O*-acetyl-3-*tert*-butoxycarbonyl-3-cyano-3-deoxy-α-*L*-arabino-pentopyranosyl)-3-ethoxycarbonyl-2-methylfuran* (**22**). — Column chromatography (1:1 hexane–ether) of the crude product gave **22**, isolated as a syrup, $[\alpha]_D^{26}$ +5.5° (*c* 1, chloroform); $\nu_{max}^{CCl_4}$ 1780, 1730, 1630, 1595, 1375, 1260, 1220, 1090, 1060, and 890 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$, 80 MHz): δ 6.70 (s, 1 H, furan H), 5.80 (d, 1 H, *J* 10.0 Hz, H-2), 5.50 (bs, 1 H, H-4), 4.46 (d, 1 H, *J* 10.0 Hz, H-1), 4.25 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 4.10 (m, 2 H, H-5*e*,5*a*), 2.57 (s, 3 H, furan Me), 2.15, 1.95 (2 s, 6 H, 2 Ac), 1.47 (s, 9 H, Me_3C), and 1.34 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O).

(*f*) *3-Acetoxy-4-*tert*-butoxycarbonyl-5-(1-*tert*-butoxycarbonyl-1-cyanomethyl)-4-cyanotetrahydropyran* (**33**). — Column chromatography (2:1 hexane–ether) of the crude product gave a mixture of the three stereoisomers **33**, isolated as a syrup; $\nu_{max}^{CCl_4}$ 1760, 1370, 1260, 1212, 1145, 1120, and 1050 cm^{-1}. ^{1}H-N.m.r. ($CDCl_3$, 80 MHz): δ 5.40–5.10 (m, 1 H, H-3), 4.25–3.0 (m, 6 H, H-2,5,6,2′,6′ and NC-CH-Boc), 2.10, 2.07, 2.05 (3 s, 3 H, Ac), 1.6–1.4 (5 s, 18 H, 2 Me_3C). The mixture of three stereoisomers **33** was dissolved in hexane, giving a solid material which had m.p. 114–116°; ν_{max}^{KBr} 1760–1740, 1370, 1275, 1215, 1152, 1025, 1060, 1050, and 824 cm^{-1}. N.m.r. data ($CDCl_3$): ^{1}H (80 MHz), δ 5.40–5.20 (m, 1 H, H-3), 4.20–3.50 (m, 5 H, H-2,6,2′,6′, NC-CH-Boc), 3.00 (m, 1 H, H-5), 2.10, 2.07 (2 s, 3 H, Ac), 1.55, 1.52, 1.50, and 1.47 (4 s, 18 H, 2 Me_3C); ^{13}C, δ 168.71, 162.97, 162.58 (COO), 113.44, 113.31, 112.73 (CN), 86.51, 86.14, 85.81, 85.39 (CMe_3), 69.64, 68.88 (C-3), 66.36, 65.67, 65.55 (C-2,6), 54.93, 48.93 (C-4), 38.95, 37.23, 36.96, 33.11 (C-5, NC-*C*H-Boc), 27.68 (Me_3C), 20.61 and 20.39 (*Me*COO) (Found: C, 58.44; H, 6.73; N, 6.54. $C_{20}H_{28}N_2O_7$ calc.: C, 58.81; H, 6.91; N, 6.85%).

(*g*) *(2R,3R,4R)-3-Acetoxy-4-*tert*-butoxycarbonyl-5-(1-*tert*-butoxycarbonyl-1-cyanomethyl)-4-cyano-2-(3-ethoxycarbonyl-2-methylfur-5-yl)tetrahydropyran* (**34**). — Column chromatography (3:1 hexane–ether) of the crude product gave the mixture of stereoisomers **34**, isolated as a syrup; $[\alpha]_D^{26}$ −29° (*c* 1, chloroform); $\nu_{max}^{CCl_4}$ 1775, 1740, 1730, 1625, 1590, 1375, 1260, 1214, 1152, and 1068 cm^{-1}. N.m.r. data ($CDCl_3$): ^{1}H (80 MHz), δ 6.67 (s, 1 H, furan H), 5.22 and 5.50 (2 d, 1 H, *J* 9.8 and 10.0 Hz, H-3), 4.57 and 4.50 (2 d, 1 H, *J* 10.0 and 9.8 Hz, H-2), 4.25 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 4.15–3.20 (m, 4 H, H-4,5,5′ and NC-CH-Boc), 2.57 (s, 3 H, furan Me), 1.97 and 1.95 (2 s, 3 H, Ac), 1.55 and 1.50 (2 s, 18 H, 2 Me_3C), and 1.32 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O); ^{13}C, δ 167.51, 163.41, 163.13, 162.80, 162.44 and 162.33 (COO), 159.82 (furan C-2), 145.91 (furan C-5), 114.20 (furan C-3), 113.50, 112.94, and 112.41 (CN), 111.11 (furan C-4), 86.06 and 85.63 (Me_3C), 71.93 (C-2), 69.49 and 69.00 (C-3), 66.43 and 65.81 (C-6), 59.98 (OCH_2CH_3), 55.65 and

54.75 (C-4), 40.11, 38.87, 37.35 and 36.80 (NC-*C*H-Boc, C-5), 28.05 Me_3C), 19.95 (*Me*COO), 14.07 and 13.43 (furan Me and CH_3CH_2O).

(*h*) *(2R,3R,4R)-3-Acetoxy-2-(3-acetyl-2-methylfur-5-yl)-4-*tert*-butoxycarbonyl-5-(1-*tert*-butoxycarbonyl-1-cyanomethyl)-4-cyanotetrahydropyran* (**35**). — Column chromatography (1:1 hexane–ether) of the crude product gave the mixture of stereoisomers **35**, isolated as a syrup, $[\alpha]_D^{30}$ −22.5° (*c* 1, chloroform); $\nu_{max}^{CCl_4}$ 1762, 1700, 1620, 1580, 1380, 1264, 1218, 1158, 1070, 948, and 837 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 5.57 and 5.52 (2 d, 1 H, *J* 10.0 Hz, H-3), 4.62 and 4.55 (2 d, 1 H, *J* 10.0 Hz, H-2), 4.30–3.80 (m, 2 H, H-6,6'), 3.55–3.37 (m, 1 H, NC-CH-Boc), 3.25–3.00 (m, 1 H, H-5), 2.57 (s, 3 H, furan Me), 2.40 (s, 3 H, furan Ac), 2.00 and 1.95 (2 s, 3 H, Ac), 1.55 and 1.50 (2 s, 18 H, 2 Me_3C); ^{13}C, δ 193.33 (CO), 167.77, 163.06, 162.70, 162.58 and 162.24 (COO), 159.27 (furan C-2), 146.33 (furan C-5), 122.04 (furan C-3), 113.77, 113.19 and 112.66 (CN), 110.88 (furan C-4), 87.32, 86.91 and 85.85 (Me_3C), 72.17 (C-2), 69.78 and 69.27 (C-3), 66.69 and 66.05 (C-6), 55.92 and 54.98 (C-4), 40.34, 39.13, 37.56, 37.04 (C-5 and NC-*C*H-Boc), 29.01 (furan Ac), 27.72 and 27.62 (Me_3C), 20.17 (*Me*COO), and 14.21 (furan Me).

Benzoylation of **6, 7, 9,** *and* **10**. — Conventional treatment of the appropriate hydroxy compound with benzoyl chloride–pyridine gave the following results:

Starting compound (g)	*Benzoyl chloride (mL)*	*Products (g, %)*
6 (0.34)	1.5	**26** (0.48, 78.3)
7 (0.25)	1.0	**27** (0.40, 86.0)
9 (0.50)	1.0	**28** (0.70, 91.7)
10 (0.14)	0.5	**29** (0.16, 72.8)

(*a*) t-*3*,t-*5*-*Dibenzoyloxy*-r-*4*-tert-*butoxycarbonyl-4-cyanotetrahydrothiopyran* (**26**). — Column chromatography (3:1 hexane–ether) of the crude product gave **26**, m.p. 138–139° (from hexane–ether); ν_{max}^{KBr} 1770–1740, 1380, 1290, 1260, 1160, 1085, 1070, 1040, 1028, 835, and 705 cm^{-1}. ^1H-N.m.r. data ($CDCl_3$): δ 8.10 and 7.50 (2 m, 10 H, 2 Ph), 5.87 (dd, 2 H, *J* 8.5 and 6.0 Hz, H-3,5), 3.0 (m, 4 H, H-2*e*,2*a*,6*e*,6*a*), and 1.25 (s, 9 H, Me_3C) (Found: C, 64.09; H, 5.37; N, 2.94. $C_{25}H_{25}NO_6S$ calc.: C, 64.23; H, 5.40; N, 3.00%).

(*b*) t-*3*,t-*5*-*Dibenzoyloxy*-r-*4*-tert-*butoxycarbonyl-4-cyanotetrahydropyran* (**27**). — Column chromatography (1:1 hexane–ether) of the crude product gave **27**, m.p. 178–179° (from ethanol); ν_{max}^{KBr} 1760, 1375, 1290, 1272, 1257, 1120, 1094, 1070, 950, 820, and 710 cm^{-1}. ^1H-N.m.r. data ($CDCl_3$): δ 8.10 and 7.50 (2 m, 10 H, 2 Ph), 5.60 (dd, 2 H, *J* 10.4 and 5.0 Hz, H-3,5), 4.25 (dd, 2 H, *J* 11.6 and 5.0 Hz, H-2*e*,6*e*), 3.70 (dd, 2 H, *J* 11.6 and 10.4 Hz, H-2*a*,6*a*), and 1.32 (s, 9 H, Me_3C) (Found: C, 66.83; H, 5.87; N, 2.99. $C_{25}H_{25}NO_7$ calc.: C, 66.50; H, 5.58; N, 3.10%).

(*c*) *5-(2,4-Di-*O*-benzoyl-3-*tert*-butoxycarbonyl-3-*C*-cyano-3-deoxy-β-*D*-xylo-pentopyranosyl)-3-ethoxycarbonyl-2-methylfuran* (**28**). — Column chromatography (3:1 hexane–ether) of the crude product gave **28**, isolated as a syrup, $[\alpha]_D^{28}$ −32° (*c*

1.3, chloroform); $\nu_{max}^{CCl_4}$ 1746, 1720, 1615, 1605, 1580, 1364, 1253, 1235, 1076, 1055, 1100, and 690 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H (80 MHz), δ 8.0 and 7.5 (2 m, 10 H, 2 Ph), 6.70 (s, 1 H, furan H), 5.90 (d, 1 H, *J* 10.0 Hz, H-2), 5.75 (dd, 1 H, *J* 10.5 and 5.0 Hz, H-4), 4.80 (d, 1 H, *J* 10.0 Hz, H-1), 4.40 (dd, 1 H, *J* 11.5 and 5.0 Hz, H-5*e*), 4.20 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 3.90 (dd, 1 H, *J* 11.5 and 10.5 Hz, H-5*a*), 2.50 (s, 3 H, furan Me), 1.30 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O), and 1.25 (s, 9 H, Me_3C); ^{13}C, δ 164.00, 163.37, 163.02, 162.14 (4 COO), 159.76 (furan C-2), 146.00 (furan C-5), 133.66, 129.67, 128.40 and 128.06 (C_6H_5COO), 114.21 (furan C-3), 113.85 (CN), 111.03 (furan C-4), 85.76 (CMe_3), 71.85, 68.93, and 68.39 (C-1,2,4), 65.43 (C-5), 59.82 (OCH_2CH_3), 57.98 (C-3), 27.00 (Me_3C), 13.95 and 13.30 (furan Me and CH_3CH_2O).

(*d*) *3-Acetyl-5-(2,4-di-O-benzoyl-3-*tert*-butoxycarbonyl-3-C-cyano-3-deoxy-β-*D*-xylo-pentopyranosyl)-2-methylfuran* (**29**). — Column chromatography (1:1 hexane–ether) of the crude product gave **29**, isolated as a syrup, $[\alpha]_D^{30}$ −35° (*c* 1, chloroform); $\nu_{max}^{CCl_4}$ 1770, 1700, 1620, 1580, 1380, 1290–1250, 1100–1070, 945, and 703 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H (80 MHz), δ 8.00 and 7.50 (2 m, 10 H, 2 Ph), 6.67 (s, 1 H, furan H), 5.90 (d, 1 H, *J* 10.0 Hz, H-2), 5.77 (dd, 1 H, *J* 10.5 and 5.5 Hz, H-4), 4.82 (d, 1 H, *J* 10.0 Hz, H-1), 4.40 (dd, 1 H, *J* 11.5 and 5.5 Hz, H-5*e*), 3.92 (dd, 1 H, *J* 11.5 and 10.5 Hz, H-5*a*), 2.50 (s, 3 H, furan Me), 2.30 (s, 3 H, furan Ac), and 1.27 (s, 9 H, Me_3C); ^{13}C, δ 193.37 (COMe), 164.19, 163.55, 162.21, (3 COO), 159.29 (furan C-2), 146.08 (furan C-5), 133.91, 129.87, 128.60 and 128.14 (C_6H_5COO), 121.90 (furan C-3), 113.98 (CN), 110.78 (furan C-4), 86.07 (CMe_3), 72.04, 69.07, and 68.50 (C-1,2,4), 65.64 (C-5), 58.05 (C-3), 28.81 (*Me*CO), 27.23 (Me_3C), and 14.08 (furan Me).

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