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SYNTHESIS OF 3-CYANO-Δ^2- AND -Δ^3-DIHYDRO-PYRAN AND -THIOPYRAN DERIVATIVES

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ABSTRACT

Treatment of *trans,trans*-3,5-diacyloxy-*r*-4-*tert*-butoxycarbonyl-4-cyano-tetrahydropyran (**1a–b**) and -tetrahydrothiopyran (**1c–d**), 5-(2,4-di-*O*-acyl-3-*tert*-butoxycarbonyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-3-ethoxycarbonyl-2-methylfuran (**2a–b**) and -3-acetyl-2-methylfuran (**2c–d**), and methyl 2,4,6-tri-*O*-acetyl-3-*tert*-butoxycarbonyl-3-cyano-3-deoxy-α-D-*gluco*-hexopyranoside (**3**) with toluene-*p*-sulfonic acid in acetic anhydride gave the corresponding branched unsaturated compounds, 5-acyl-4-cyano-5,6-dihydro-2*H*-pyran (**4a–b**) and -thiopyran (**4c–d**), 5-(4-*O*-acyl-3-cyano-2,3-dideoxy-β-D-*glycero*-pent-2-enopyranosyl)-furans (**5a–d**) (minor), 5-(2-*O*-acyl-3-cyano-3,4-dideoxy-β-D-*glycero*-pent-3-enopyranosyl)furans (**6a–d**) (major), and methyl 2,6-di-*O*-acetyl-3-cyano-3,4-dideoxy-α-D-*erythro*-hex-3-enopyranoside (**7**).

INTRODUCTION

We have reported on the synthesis and reactivity 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[1–3]. When *tert*-butyl cyanoacetate is used, products can be transformed into branched, unsaturated *C*- or *O*-glycosyl derivatives by acid-catalysed loss of the *tert*-butoxycarbonyl group.

This reaction has now been applied to **1a–d, 2a–d**, and **3** obtained[3] by the reaction of *tert*-butyl cyanoacetate variously with diglycolaldehyde, thiodiglycolaldehyde, (2*S*)-2-(3-ethoxycarbonyl-2-methyl-5-furyl)-3,5-dihydroxy-1,4-dioxane, (2*S*,3*R*,5*S*)-2-(3-acetyl-2-methyl-5-furyl)-3,5-dihydroxy-1,4-dioxane, and α-(*S*)-methoxy-α′-(*R*)-hydroxymethyldiglycolaldehyde.

RESULTS AND DISCUSSION

The reaction was carried out in boiling acetic anhydride, using toluene-*p*-sulfonic acid as catalyst, and the products were isolated by column chromatography.

The pyrans **1a,b** and the thiopyrans **1c,d** gave the 5-acyl-4-cyano-5,6-dihydro-

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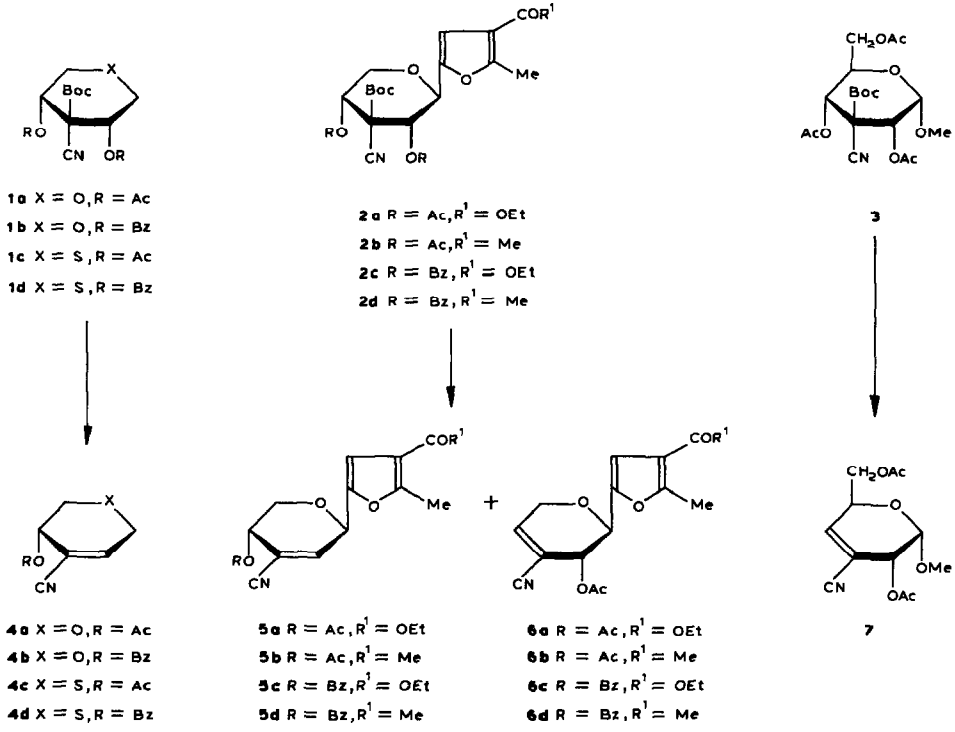
2*H*-pyrans (**4a,b**) and -thiopyrans (**4c,d**), respectively. With the *C*-pyranosyl derivatives **2a–d**, the major products were 5-(2-*O*-acyl-3-cyano-3,4-dideoxy-β-D-*glycero*-pent-3-enopyranosyl)furans (**6a–d**), and the minor products were 5-(4-*O*-acyl-3-cyano-2,3-dideoxy-β-D-*glycero*-pent-2-enopyranosyl)furans (**5a–d**). The sole product from **3** was methyl 2,6-di-*O*-acetyl-3-cyano-3,4-dideoxy-α-D-*erythro*-hex-3-enopyranoside (**7**).

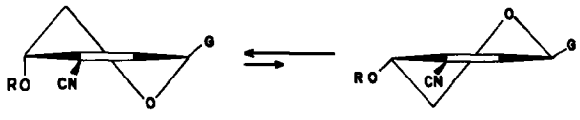


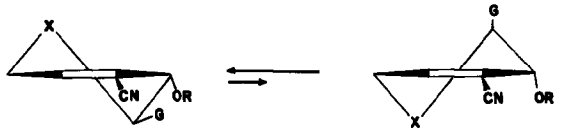
The structures of **4a–d, 5a–d, 6a–d**, and **7** were established on the basis of elemental analyses and spectroscopic data. Thus, **4a–d, 5a–d, 6a–d**, and **7** show characteristic i.r. bands[4] for alkene, ester, and α,β-unsaturated nitrile groups. The mass spectra of **4a,c,d, 6b,d**, and **7** contained stronger peaks for ($M^+ + 1$) ions than for molecular ions, as has been reported[5].

The half-chair form is assumed, as reported[6–11] for other dihydropyran derivatives. Compounds **4a,b** had $J_{5,6} + J_{5,6'}$ 6.1 and 6.6 Hz, respectively (see Table II), which accord[12] with an almost exclusive ^6H_O conformation (**8A**). This is also in agreement[13] with the $J_{3,5}$ values of 0.7 Hz. The allylic effect[6] favours conformers ^6H_O. In contrast, **4c,d** had $J_{5,6} + J_{5,6'}$ 12.0 and 11.5 Hz, respectively (see Table II), suggesting[12] a ~2:1 equilibrium of the half-chair forms $^SH_6$ (**9A**) and ^6H_S (**9B**), probably due to the "hockey-stick" effect[14]. Compounds **5a–d** had $J_{4,5} + J_{4,5'}$ 6.3–6.5 Hz, and $J_{2,4}$ <0.7 Hz (see Table IV) in agreement with the preferred

$^5H_0$(D) conformers (**8A**). This conformation is stabilised by the allylic effect. Compounds **6a–d** had $J_{4,5} + J_{4,5'}$ 5.0–5.6, $J_{2,4}$ values 1.0–1.5, $J_{2,5}$ 2.4, and $J_{1,2}$ 6.0–6.5 Hz (see Table IV), indicating a preference for the $^OH_1$(D) conformation (**9A**).

The homoallylic $J_{2,5}$ value of 3.5 Hz (both protons quasi-diaxial)[12,15] for **7**, the allylic $J_{2,4}$ value of 2.3 Hz (quasi-axial allylic proton), and the $J_{1,2}$ value of 4.0 Hz





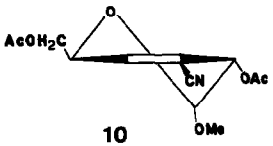


TABLE I

^{1}H-N.M.R. CHEMICAL SHIFTS (δ p.p.m.)[a] FOR **4a–d**

Compound	*H-2*	*H-2'*	*H-3*	*H-5*	*H-6*	*H-6'*	*Others*
4a[b]	4.30ddd	4.16dt	6.90ddd	5.21m	3.86dd	3.75dd	2.09 (s, 3 H, Ac)
4b[b]	4.40ddd	4.25dt	6.98ddd	5.49m	4.02dd	3.92dd	8.10 and 7.5 (2 m, 5 H, Ph)
4c[c]	←3.30m→		6.95dt	5.50m	3.00dd	2.80dd	2.17 (s, 3 H, Ac)
4d[c]	←3.60–3.10m→		6.95dt	5.70m	3.10dd	2.80dd	8.10 and 7.5 (2 m, 5 H, Ph)

[a]For solutions in $CDCl_3$ (internal Me_4Si). [b]200 MHz. [c]80 MHz.

TABLE II

PROTON-PROTON COUPLING CONSTANTS[a] (Hz) FOR **4a–d**

Compound	$J_{2,2'}$	$J_{2,3}$	$J_{2',3}$	$J_{2,5}$	$J_{2',5}$	$J_{3,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
4a	19.3	3.4	2.4	1.3	2.4	0.7	2.9	3.2	12.7
4b	19.3	3.3	2.4	1.4	2.4	0.7	3.2	3.4	12.6
4c	19.0	4.0	4.0	2.5	2.0	1.5	5.0	7.0	13.5
4d	19.0	3.5	3.5	2.5	1.5	1.6	4.5	7.0	13.5

[a]A series decoupling experiments enabled assignments to be made.

TABLE III

^{1}H-N.M.R. CHEMICAL SHIFTS (δ, p.p.m.)[a] FOR **5a–d, 6a–d,** AND **7**

Compound	*H-2*	*H-1*	*H-4*	*H-5*	*H-5'*	*Others*
5a[b]	6.95bd	←5.35m→		4.0dd	3.8dd	6.57 (s, 1 H, furan H-4), 4.25 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 2.6 (s, 3 H, furan Me-2), 2.17 (s, 3 H, Ac), and 1.35 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O)
5b[b]	6.90dd	←5.30–5.15m→		3.95dd	3.85dd	6.57 (s, 1 H, furan H-4), 2.60 (s, 3 H, furan Me-2), 2.40 (s, 3 H, furan Ac-3), and 2.17 (s, 3 H, Ac)
5c[b]	7.0dd	5.45d	5.55m	4.2dd	3.95dd	8.10 and 7.50 (2 m, 5 H, Ph), 6.62 (s, 1 H, furan H-4), 4.30 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 2.60 (s, 3 H, furan Me-2), and 1.35 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O)
5d[b]	7.0bd	5.45d	5.55m	4.15dd	3.95dd	8.10 and 7.50 (2 m, 5 H, Ph), 6.7 (s, 1 H, furan H-4), 2.60 (s, 3 H, furan Me-2), and 2.40 (s, 3 H, furan Ac-3)
6a[c]	5.70m	4.63d	6.88dt	4.42dt	4.30dt	6.61 (s, 1 H, furan H-4), 4.25 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 2.55 (s, 3 H, furan Me-2), 2.1 (s, 3 H, Ac), and 1.32 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O)
6b[c]	5.67m	4.54d	6.84dt	4.38dt	4.25dt	6.55 (s, 1 H, furan H-4), 2.60 (s, 3 H, furan Me-2), 2.40 (s, 3 H, furan Ac-3), and 2.12 (s, 3 H, Ac)
6c[b]	6.0m	4.86d	6.95dt	←4.40m→		8.10 and 7.50 (2 m, 5 H, Ph), 6.67 (s, 1 H, furan H-4), 4.3 (q, 2 H, *J* 7.0 Hz, CH_3CH_2O), 2.55 (s, 3 H, furan Me-2), and 1.32 (t, 3 H, *J* 7.0 Hz, CH_3CH_2O)
6d[b]	6.0m	4.80d	6.95dt	←4.40m→		8.10 and 7.50 (2 m, 5 H, Ph), 6.65 (s, 1 H, furan H-4), 2.55 (s, 3 H, furan Me-2), and 2.35 (s, 3 H, furan Ac-3)
7[c]	5.41–5.36td	5.13d	6.71pseudot	4.47m	—	4.3 (dd, 1 H, *J* 11.5, 5.0 Hz, H-6), 4.22 (dd, 1 H, *J* 11.5, 5.0 Hz, H-6'), 3.49 (s, 3 H, MeO), 2.20 and 2.11 (2 s, 6 H, 2 Ac)

[a]For solutions in $CDCl_3$ (internal Me_4Si). [b]80 MHz. [c]200 MHz.

TABLE IV

PROTON–PROTON COUPLING CONSTANTS[a] (Hz) FOR COMPOUNDS **5a–d, 6a–d,** AND **7**

Compound	$J_{1,2}$	$J_{2,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	$J_{2,5}$
5a	3.0	<0.7	3.0	3.3	10.0	—
5b	3.5	<0.7	3.0	3.4	13.0	—
5c	3.5	<0.7	3.0	3.5	9.0	—
5d	3.0	<0.7	3.0	3.5	12.5	—
6a	6.0	1.3	2.8	2.8	19.5	2.4
6b	6.5	1.4	2.7	2.7	19.4	2.4
6c	6.0	1.5	2.7	2.7	—	—
6d	6.5	1.0	2.5	2.5	—	—
7	4.0	2.3	1.8	—	—	3.5

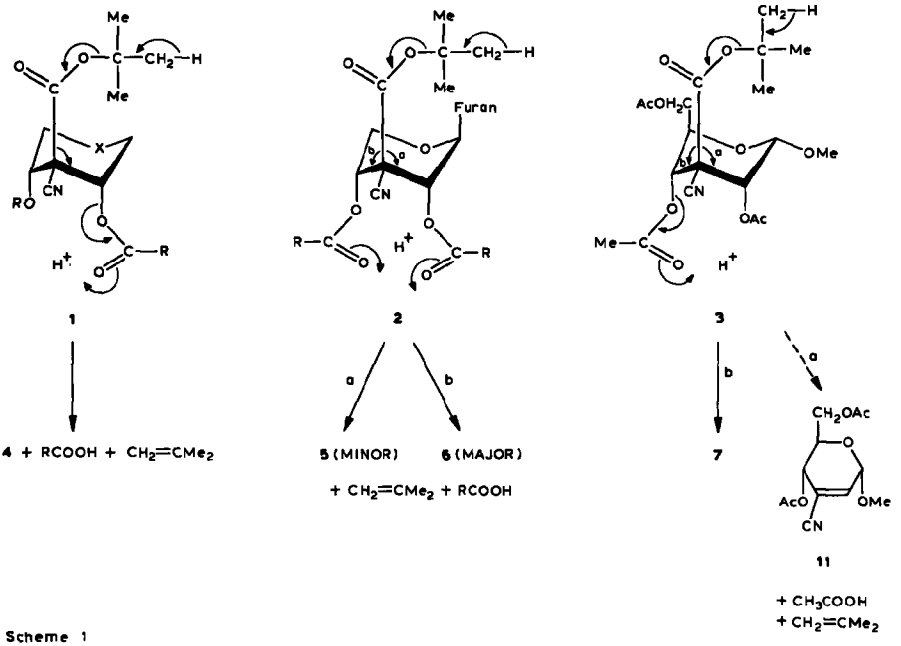
[a]A series of decoupling experiments enabled assignments to be made.

(see Table IV) (quasi-axial-equatorial) accord with the $^{O}H_{1}$(D) conformation **10**. This conformational preference is determined by the anomeric effect[16] in competition with the allylic effect[6].

The ^{13}C-n.m.r. data (see Experimental) of **4a–d, 5a–d, 6a–d,** and **7** accord with the assigned structures.

Both **5a** and **6a** were unaffected on treatment with acetic anhydride–acid.

Scheme 1 shows the *trans*-elimination yielding the products **4–7**. The *meso* compounds **1a–d** yielded the racemic products **4a–d**. However, *trans*-elimination in the chiral compounds **2a–d** yielded **5a–d** and **6a–d** as minor and major products,



Scheme 1

respectively. The chiral compound **3** gave only one of the two possible isomers **7**. This finding accords with results[7] on similar reactions of nitro compounds, which were ascribed to the electron-withdrawing effect of the glycosidic center and to the $A^{1,2}$ effect[17] of the nitro group. For the cyano compounds, only the first of these effects may be operative.

The structures of the products of the elimination reaction **4–7** confirmed the configurations at C-4 (**1a–d**) and C-3 (**2a–d,3**) that were previously tentatively assigned[3].

EXPERIMENTAL

The general methods have been described[18]. N.m.r. spectra (^1H at 80 and 200 MHz, ^{13}C at 20 MHz) were obtained with Bruker WP-80-SY and WP-200 spectrometers. Mass spectra (70 eV) were recorded with an AEI MS/30-VG spectrometer.

Reaction of **1a–d, 2a–d,** *and* **3** *with acetic anhydride and toluene-*p*-sulfonic acid.* — A mixture of **1a–d, 2a–d,** or **3**, acetic anhydride, and toluene-*p*-sulfonic acid (<5 mg) was stirred and boiled under reflux. Chloroform (75 mL) was added, and the mixture was washed with saturated aqueous $NaHCO_3$ (5 × 50 mL) and then water (25 mL), dried, filtered, and concentrated.

The following conditions were used:

Starting compound (g)	*Ac_2O (mL)*	*Time (h)*	*Product (g, %)*
1a (0.4)	6	3	**4a** (0.17, 83.3)
1b (2.5)	10	3	**4b** (0.43, 33.8)
1c (0.9)	10	3	**4c** (0.32, 67.5)
1d (1.61)	10	3	**4d** (0.62, 72.8)
2a (0.6)	7	3	**5a** (0.09, 22.5)
			6a (0.23, 57.5)
2b (0.7)	7	3	**5b** (0.07, 15.5)
			6b (0.3, 66.5)
2c (1.2)	7	5	**5c** (0.1, 13.2)
			6c (0.39, 51.4)
2d (0.78)	7	3	**5d** (0.1, 20.9)
			6d (0.15, 31.4)
3 (0.7)	7	3	**7** (0.35, 79.7)

(a) With trans,trans-*3,5-diacetoxy-*r*-4-*tert*-butoxycarbonyl-4-cyanotetrahydropyran*[3] **(1a)**. Column chromatography (1:2 hexane–ether) of the crude product gave 5-acetoxy-4-cyano-5,6-dihydro-2*H*-pyran (**4a**), isolated as a syrup; ν_{max}^{film} 3035, 2225, 1738, 1642, 1224, 1134, 1095, 1041, and 860 cm^{-1}. N.m.r. data: ^1H, see Tables I and II; ^{13}C, 169.84 (COO), 147.42 (C-3), 115.78 (CN), 110.19 (C-4), 66.74, 64.70 (C-2,6), 63.01 (C-5), and 20.54 (MeCOO). Mass spectrum: *m/z* 168 (M^+ +1), 167 (M^+), 140 (M^+ − CNH), 139 (M^+ − CNH, H), 108 (M^+ − $C_2H_4O_2$), and 98 (M^+ − CN, $C_2H_3O_2$) (Found: C, 57.60; H, 5.71; N, 8.10. $C_8H_9NO_3$ calc.: C, 57.47; H, 5.42; N, 8.38%).

(b) With trans,trans-*3,5-dibenzoyloxy*-r-*4*-tert-*butoxycarbonyl-4-cyanotetrahydropyran*[3] (**1b**). Column chromatography (1:2 hexane–ether) of the crude product gave 5-benzoyloxy-4-cyano-5,6-dihydro-2*H*-pyran (**4b**), m.p. 80–81° (from hexane–ether); ν_{max}^{KBr} 3064, 2225, 1713, 1650, 1602, 1286, 1262, 1106, 1036, 861, 819, and 707 cm^{-1}. N.m.r. data: ^1H, see Tables I and II; ^{13}C, δ 165.64 (COO), 147.58 (C-3), 133.54, 129.88, 129.07, 128.47 (C_6H_5COO), 115.94 (CN), 110.51 (C-4), 66.95, 64.86, and 63.75 (C-2,5,6). (Found: C, 68.02; H, 4.96; N, 5.86. $C_{13}H_{11}NO_3$ calc.: C, 68.11; H, 4.83; N, 6.11%).

(c) With trans,trans-*3,5-diacetoxy*-r-*4*-tert-*butoxycarbonyl-4-cyanotetrahydrothiopyran*[3] (**1c**). Column chromatography (2:1 hexane–ether) of the crude product gave 5-acetoxy-4-cyano-5,6-dihydro-2*H*-thiopyran (**4c**), isolated as a syrup; ν_{max}^{film} 3040, 2227, 1742, 1637, 1224, 1030, 990, 923, and 803 cm^{-1}. N.m.r. data: ^1H, see Tables I and II; ^{13}C, δ 169.33 (COO), 145.32 (C-3), 116.30, 114.33 (CN, C-4), 63.75 (C-5), 27.94, 25.26 (C-2,6), and 20.36 (MeCOO). Mass spectrum: *m/z* 184 ($M^+ + 1$), 183 (M^+), 140 ($M^+ - C_2H_3O$), 124 ($M^+ - C_2H_3O_2$), 123 ($M^+ - C_2H_4O_2$), and 122 ($M^+ - C_2H_4O_2 - H$) (Found: C, 52.70; H, 5.17; N, 7.47. $C_8H_9NO_2S$ calc.: C, 52.44; H, 4.95; N, 7.64%).

(d) With trans,trans-*3,5-dibenzoyloxy*-r-*4*-tert-*butoxycarbonyl-4-cyanotetrahydrothiopyran*[3] (**1d**). Column chromatography (3:1 hexane–ether) of the crude product gave 5-benzoyloxy-4-cyano-5,6-dihydro-2*H*-thiopyran (**4d**), isolated as a syrup; ν_{max}^{film} 3061, 2227, 1722, 1638, 1601, 1583, 1263, 1095, 891, 803, and 712 cm^{-1}. N.m.r. data: ^1H, see Tables I and II; ^{13}C, δ 164.77 (COO), 145.50 (C-3), 133.08, 129.29, 128.64, 128.06 (C_6H_5COO), 116.35, 114.08 (CN, C-4), 64.39 (C-5), 27.86 and 25.16 (C-2,6). Mass spectrum: *m/z* 246 ($M^+ + 1$), 245 (M^+), 140 ($M^+ - C_7H_5O$), 124 ($M^+ - C_7H_6O_2$), 123 ($M^+ - C_7H_6O_2 - H$), 105 ($M^+ - C_6H_6NOS$) (Found: C, 63.85; H, 4.60; N, 5.92. $C_{13}H_{11}NO_2S$ calc.: C, 63.65; H, 4.52; N, 5.71%).

*(e) With 5-(2,4-di-*O*-acetyl-3-*tert-*butoxycarbonyl-3-cyano-3-deoxy-β-*D*-xylo-pentopyranosyl)-3-ethoxycarbonyl-2-methylfuran*[3] (**2a**). Column chromatography (1:1 hexane–ether) of the crude product gave, first, 5-(4-*O*-acetyl-3-cyano-2,3-dideoxy-β-D-*glycero*-pent-2-enopyranosyl)-3-ethoxycarbonyl-2-methylfuran (**5a**), m.p. 109–110° (from hexane), $[\alpha]_D^{15}$ +98° (*c* 1, chloroform); ν_{max}^{KBr} 3058, 3035, 2234, 1743, 1721, 1611, 1570, 1232, 1087, and 780 cm^{-1}. N.m.r. data: ^1H, see Tables III and IV; ^{13}C, δ 169.98, 163.39 (2 COO), 160.64 (furan C-2), 146.08 (furan C-5), 144.95 (C-2), 115.60, 114.59, 111.82 (CN, C-3, furan C-3), 111.82 (furan C-4), 67.74, 62.65 (C-1,4), 63.44 (C-5), 60.43 (CH_3CH_2O), 20.76 (*Me*COO), 14.35, and 13.83 (furan Me, CH_3CH_2O) (Found: C, 59.92; H, 5.70; N, 4.22. $C_{16}H_{17}NO_6$ calc.: C, 60.18; H, 5.36; N, 4.38%).

Eluted second was 5-(2-*O*-acetyl-3-cyano-3,4-dideoxy-β-D-*glycero*-pent-3-enopyranosyl)-3-ethoxycarbonyl-2-methylfuran (**6a**), m.p. 99–100° (from hexane), $[\alpha]_D^{15}$ −123° (*c* 1, chloroform); ν_{max}^{KBr} 3065, 3037, 2224, 1748, 1719, 1640, 1616, 1572, 1247, 1230, 1090, 1054, and 768 cm^{-1}. N.m.r. data: ^1H, see Tables III and IV; ^{13}C, δ 169.34, 163.38 (2 COO), 160.04 (furan C-2), 164.57 (furan C-5), 145.76 (C-4),

115.16, 114.43 (CN, furan C-3), 111.30 (C-3), 110.71 (furan C-4), 70.76, 63.70 (C-1,2), 63.93 (C-5), 60.25 (CH_3CH_2O), 20.48 (*Me*COO), 14.25, and 13.72 (CH_3CH_2O, and furan Me) (Found: C, 60.20; H, 4.98; N, 4.35. $C_{16}H_{17}NO_6$ calc.: C, 60.18; H, 5.36; N, 4.38%).

*(f) With 3-acetyl-5-(2,4-di-*O*-acetyl-3-*tert*-butoxycarbonyl-3-cyano-3-deoxy-β-*D*-xylo-pentopyranosyl)-2-methylfuran*[3] (**2b**). Column chromatography (2:1 hexane–ether) of the crude product gave, first, 3-acetyl-5-(4-*O*-acetyl-3-cyano-2,3-dideoxy-β-D-*glycero*-pent-2-enopyranosyl)-2-methylfuran (**5b**), isolated as a syrup, $[\alpha]_D^{15}$ +67° (*c* 1, chloroform); ν_{max}^{film} 3030, 2228, 1742, 1676, 1595, 1560, 1227, 1090, 1050, and 735 cm^{-1}. N.m.r. data: ^1H, see Tables III and IV; ^{13}C, δ 193.44 (CO), 169.93 (COO), 159.75 (furan C-2), 146.19 (furan C-5), 144.84 (C-2), 122.18 (furan C-3), 115.53 (CN), 112.81 (C-3), 111.26 (furan C-4), 67.73, 62.54 (C-1,4), 63.49 (C-5), 29.04 (furan Ac), 20.69 (*Me*COO), and 14.40 (furan Me). Mass spectrum: *m/z* 289 (M^+), 230 ($M^+ - C_2H_3O_2$), 229 ($M^+ - C_2H_4O_2$), 228 ($M^+ - C_2H_4O_2 - H$), 214 ($M^+ - C_2H_4O_2 - CH_3$), 202 ($M^+ - C_2H_4O_2 - CNH$), and 186 ($M^+ - C_2H_4O_2 - C_2H_3O$) (Found: C, 62.10; H, 5.43; N, 5.05. $C_{15}H_{15}NO_5$ calc.: C, 62.27; H, 5.22; N, 4.84%).

Eluted second was 3-acetyl-5-(2-*O*-acetyl-3-cyano-3,4-dideoxy-D-*glycero*-pent-3-enopyranosyl)-2-methylfuran (**6b**), isolated as a syrup, $[\alpha]_D^{15}$ −104° (*c* 1, chloroform); ν_{max}^{film} 3060, 3010, 2227, 1749, 1677, 1605, 1565, 1222, 1119, 1044, 949, 831, and 756 cm^{-1}. N.m.r. data: ^1H, see Tables III and IV; ^{13}C, δ 193.24 (CO), 169.16 (COO), 158.94 (furan C-2), 146.84 (furan C-5), 145.78 (C-4), 121.86 (furan C-3), 114.95 (CN), 110.23 (C-3), 110.01 (furan C-4), 70.47, 63.45 (C-1,2), 63.98 (C-5), 28.75 (furan Ac), 20.24 (*Me*COO), and 14.06 (furan Me). Mass spectrum: *m/z* 290 ($M^+ + 1$), 289 (M^+), 274 ($M^+ - CH_3$), 230 ($M^+ - C_2H_3O_2$), 229 ($M^+ - C_2H_4O_2$), 228 ($M^+ - C_2H_4O_2 - H$), 214 ($M^+ - C_2H_4O_2 - CH_3$), 202 ($M^+ - C_2H_4O_2 - CNH$), and 186 ($M^+ - C_2H_4O_2 - C_2H_3O$) (Found: C, 62.58; H, 5.45; N, 4.50. $C_{15}H_{15}NO_5$ calc.: C, 62.27; H, 5.22; N, 4.84%).

*(g) With 5-(2,4-di-*O*-benzoyl-3-*tert*-butoxycarbonyl-3-cyano-3-deoxy-β-*D*-xylo-pentopyranosyl)-3-ethoxycarbonyl-2-methylfuran*[3] (**2c**). Column chromatography (1:1 hexane–ether) of the crude product gave, first, 5-(4-*O*-benzoyl-3-cyano-2,3-dideoxy-β-D-*glycero*-pent-2-enopyranosyl)-3-ethoxycarbonyl-2-methylfuran (**5c**), isolated as a syrup, $[\alpha]_D^{15}$ +61° (*c* 1, chloroform); ν_{max}^{film} 3040, 2229, 1717, 1606, 1592, 1263, 1232, 1086, 780, and 712 cm^{-1}. N.m.r. data: ^1H, see Tables III and IV; ^{13}C, δ 165.64, 163.37 (2 COO), 160.57 (furan C-2), 146.13 (furan C-5), 145.14 (C-2), 133.64, 129.98, 129.0, 128.52 (C_6H_5COO), 115.59, 114.55, 112.87 (CN, furan C-3, C-3), 111.76 (furan C-4), 67.83, 63.22 (C-1,4), 63.62 (C-5), 60.38 (CH_3CH_2O), 14.29, and 13.78 (furan Me, CH_3CH_2O). Mass spectrum: *m/z* 381 (M^+), 336 ($M^+ - C_2H_5O$), 276 ($M^+ - C_7H_5O$), 260 ($M^+ - C_7H_6O_2$), 259 ($M^+ - C_7H_6O_2 - H$), 230 ($M^+ - C_2H_5O - C_7H_6O$), 214 ($M^+ - C_7H_6O_2 - C_2H_5O$), and 186 ($C_{11}H_6O_3$) (Found: C, 66.39; H, 5.22; N, 3.54. $C_{21}H_{19}NO_6$ calc.: C, 66.13; H, 5.02; N, 3.67%).

Eluted second was 5-(2-*O*-benzoyl-3-cyano-3,4-dideoxy-β-D-*glycero*-pent-3-

enopyranosyl)-3-ethoxycarbonyl-2-methylfuran (**6c**), isolated as a syrup, $[\alpha]_D^{15}$ −130° (*c* 1, chloroform); ν_{max}^{film} 3060, 2227, 1720, 1620, 1605, 1582, 1260, 1230, 1090, 916, 780, and 716 cm^{-1}. N.m.r. data: ^1H, see Tables III and IV; ^{13}C, δ 163.36 (2 COO), 159.99 (furan C-2), 146.60 (furan C-5), 146.20 (C-4), 133.61, 129.88, 128.77, 128.41 (C_6H_5COO), 115.25, 114.37 (CN, furan C-3), 110.71 (C-3, furan C-4), 70.86, 64.34 (C-1,2), 63.76 (C-5), 60.20 (CH_3CH_2O), 14.18, and 13.68 (furan Me, CH_3CH_2O). Mass spectrum: *m/z* 381 (M^+), 336 ($M^+ - C_2H_5O$), 260 ($M^+ - C_7H_6O_2$), 259 ($M^+ - C_7H_6O_2 - H$), 230 ($M^+ - C_2H_5O - C_7H_6O$), 214 ($M^+ - C_7H_6O_2 - C_2H_5O$), and 186 ($C_{11}H_6O_3$) (Found: C, 65.87; H, 5.29; N, 3.85. $C_{21}H_{19}NO_6$ calc.: C, 66.13; H, 5.02; N, 3.67%).

*(h) With 3-acetyl-5-(2,4-di-*O*-benzoyl-3-*tert*-butoxycarbonyl-3-cyano-3-deoxy-β-*D*-xylo-pentopyranosyl)-2-methylfuran*[3] (**2d**). Column chromatography (3:1 hexane–ether) of the crude product gave, first, 3-acetyl-5-(4-*O*-benzoyl-3-cyano-2,3-dideoxy-β-*D*-*glycero*-pent-2-enopyranosyl)-2-methylfuran (**5d**), isolated as a syrup, $[\alpha]_D^{15}$ +87° (*c* 1, chloroform); ν_{max}^{film} 3062, 2230, 1722, 1676, 1600, 1560, 1264, 1230, 1106, 1087, 946, 737, and 713 cm^{-1}. N.m.r. data: ^1H, see Tables III, IV; ^{13}C, δ 193.38 (CO), 165.57 (COO), 159.70 (furan C-2), 146.24 (furan C-5), 145.03 (C-2), 133.66, 129.90, 128.88, 128.44 (C_6H_5COO), 122.16 (furan C-3), 115.54 (CN), 112.92 (C-3), 111.23 (furan C-4), 67.83, 63.11 (C-1,4), 63.69 (C-5), 29.03 (furan Ac), and 14.36 (furan Me). Mass spectrum: *m/z* 351 (M^+), 336 ($M^+ - CH_3$), 230 ($M^+ - C_7H_5O_2$), 229 ($M^+ - C_7H_6O_2$), 214 ($M^+ - C_7H_6O_2 - CH_3$), 202 ($M^+ - C_7H_6O_2 - CNH$), and 186 ($C_{11}H_6O_3$) (Found: C, 68.60; H, 5.07; N, 4.22. $C_{20}H_{17}NO_5$ calc.: C, 68.36; H, 4.87; N, 3.98%).

Eluted second was 3-acetyl-5-(2-*O*-benzoyl-3-cyano-3,4-dideoxy-β-*D*-*glycero*-pent-3-enopyranosyl)-2-methylfuran (**6d**), isolated as a syrup, $[\alpha]_D^{15}$ −124° (*c* 1, chloroform); ν_{max}^{film} 3070, 2227, 1725, 1676, 1601, 1563, 1263, 1108, 1072, 948, 828, 760, and 715 cm^{-1}. N.m.r. data: ^1H, see Tables III and IV; ^{13}C, δ 193.38 (CO), 165.07 (COO), 159.13 (furan C-2), 146.73 (furan C-5), 146.08 (C-4), 133.61, 129.78, 128.60, 128.40 (C_6H_5COO), 122.02 (furan C-3), 115.12 (CN), 111.17 (C-3), 110.19 (furan C-4), 70.82, 64.23 (C-1,2), 64.06 (C-5), 28.88 (furan Ac), and 14.09 (furan Me). Mass spectrum: *m/z* 352 ($M^+ + 1$), 351 (M^+), 336 ($M^+ - CH_3$), 230 ($M^+ - C_7H_5O_2$), 229 ($M^+ - C_7H_6O_2$), 214 ($M^+ - C_7H_6O_2 - CH_3$), 202 ($M^+ - C_7H_6O_2 - CNH$), and 186 ($C_{11}H_6O_3$) (Found: C, 68.65; H, 4.93; N, 4.25. $C_{20}H_{17}NO_5$ calc.: C, 68.36; H, 4.87; N, 3.98%).

*(i) With methyl 2,4,6-tri-*O*-acetyl-3-*tert*-butoxycarbonyl-3-cyano-3-deoxy-α-*D*-gluco-hexopyranoside*[3] (**3**). Column chromatography (1:2 hexane–ether) of the crude product gave methyl 2,6-di-*O*-acetyl-3-cyano-3,4-dideoxy-α-*D*-*erythro*-hex-3-enopyranoside (**7**), isolated as a syrup, $[\alpha]_D^{15}$ +88° (*c* 1, chloroform); ν_{max}^{film} 3080, 2229, 1743, 1643, 1223, 1148, 1041, and 916 cm^{-1}. N.m.r. data: ^1H, see Tables III and IV; ^{13}C, δ 170.19, 169.66 (2 COO), 143.56 (C-4), 114.49 (CN), 111.13 (C-3), 94.86 (C-1), 66.49, 63.81 (C-2,5), 63.70 (C-6), 56.01 (MeO), 20.40 and 20.30 (2 *Me*COO). Mass spectrum: *m/z* 270 ($M^+ + 1$), 269 (M^+), 238 ($M^+ - CH_3O$), 210 ($M^+ - C_2H_3O_2$), 196 ($M^+ - C_3H_5O_2$), 178 ($M^+ - C_2H_4O_2 - CH_3O$),

150 ($M^{\dagger} - C_2H_4O_2 - C_2H_3O_2$), and 136 ($M^{\dagger} - C_3H_5O_2 - C_2H_4O_2$) (Found: C, 53.85; H, 5.76; N, 5.32. $C_{12}H_{15}NO_6$ calc.: C, 53.52; H, 5.61; N, 5.20%).

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