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Preparation of *C*-(2-deoxyhex/pent-1-enopyranosyl)heterocycles †

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ABSTRACT

Acetylated 1-cyanoglycals (2,6-anhydro-3-deoxyhept/hex-2-enononitriles) were prepared by direct elimination of acetic acid from the appropriate acetylated 2,6-anhydrohept/hexononitriles with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in aprotic solvents. Heterocyclisation of the cyano group of acetylated 1-cyano-D-galactal with 2-aminothiophenol led to 2-(3,4,6-tri-*O*-acetyl-2-deoxy-D-*lyxo*-hex-1-enopyranosyl)benzothiazole. Several 2-(per-*O*-acetylhexo/pentopyranosyl)benzothiazoles also gave 2-(per-*O*-acetyl-2-deoxyhex/pent-1-enopyranosyl)benzothiazoles with DBU. 3-(Per-*O*-acetylhexo/pentopyranosyl)-[1,2,4]triazolo[4,3-*a*]pyrimidines rearranged with DBU to the corresponding acetylated 2-glycosyl-[1,2,4]triazolo[1,5-*a*]pyrimidines. By the reaction of 1-cyano-D-galactal with ammonium azide, 2-(3,4,6-tri-*O*-acetyl-2-deoxy-D-*lyxo*-hex-1-enopyranosyl)tetrazole was prepared and then transformed with carboxylic acid derivatives into 2-(3,4,6-tri-*O*-acetyl-2-deoxy-D-*lyxo*-hex-1-enopyranosyl)-5-substituted-1,3,4-oxadiazoles.

INTRODUCTION

C-Nucleosides, because of their wide range of biological activity, attracted much attention during the past decades. Many efforts have been devoted to syntheses of isolated natural products, their analogues with modifications in the sugar and/or heterocyclic parts of the molecules, as well as their precursors[1–5]. However, *C*-nucleoside analogues possessing a 1′,2′-double-bond as in **A** are relatively unknown: (2-deoxyhex-1-enopyranosyl)-benzenes[6,7] and -[1,2,4]triazolo[1,5-*a*]pyridines[8], 2-(2-deoxypent-1-enopyranosyl)thiazoles[9], and several *C*-(2-deoxypent-1-enofuranosyl)heterocycles[10–13] have been described. During the preparation of this manuscript, a paper[20] describing an acetylated 5-(2-deoxy-D-*arabino*-hex-1-enopyranosyl)tetrazole was published. Some of these appear only as byproducts[8,10–12] of diverse reactions conducted under basic conditions. Very little information is

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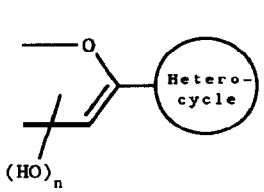
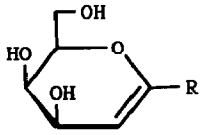


A



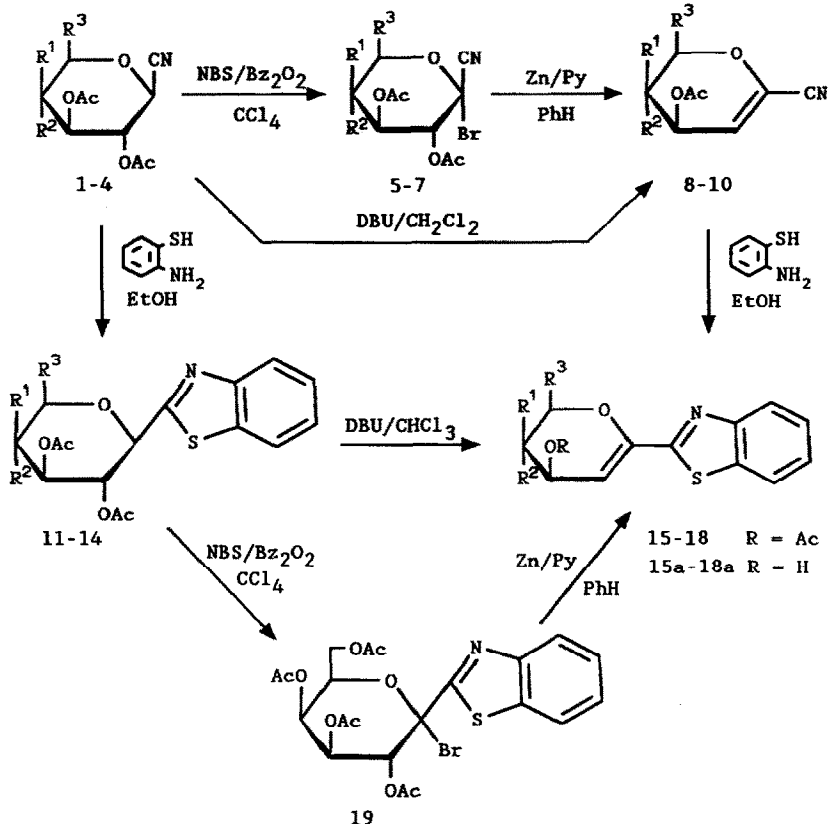
B

available on the biological activity of these compounds: cytotoxicity has been reported in two cases[8,13].

2,6-Anhydro-3-deoxy-*aldehydo*-D-*lyxo*-hept-2-enose (**B**: R = CHO) and 2,6-anhydro-3-deoxy-D-*lyxo*-hept-2-enitol (**B**: R = CH_2OH) were synthesised and probed for β-D-galactosidase inhibitory activity as analogues of the strong inhibitor 1,5-anhydro-2-deoxy-D-*lyxo*-hex-1-enitol (D-galactal, **B**: R = H)[14]. Although the above compounds proved ineffective as compared to D-galactal[14], molecules of type **A** and **B** (R = *C*-substituent) may still be interesting for testing their glycosidase inhibitory capacity. Since the inhibition may not only be due to the half-chair conformation of the sugar moiety, but other factors, e.g., basic sites and/or hydrophobicity of the aglycon, may also be important[15], we decided to prepare several compounds of type **A**. Results of glycosidase inhibition studies will be reported separately.

RESULTS AND DISCUSSION

For the preparation of the target compounds, the recently described acetylated 2,6-anhydro-3-deoxyhept/hex-2-enononitriles[16] (1-cyanoglycals, e.g., **8–10**) were chosen as starting materials. However, for multistep syntheses, it seemed advantageous to simplify their preparation; therefore, direct elimination of acetic acid from the easily accessible acetylated 2,6-anhydrohept/hexononitriles[17] (β-D-glycopyranosyl cyanides, e.g., **1–4**) was attempted. No reaction took place in pyridine–acetic acid[14], but use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in aprotic solvents (chloroform, dichloromethane, benzene) indeed gave the expected 1-cyanoglycals. Their yields (40% for **8**, 51% for **9** and **10**) were nevertheless far from satisfactory, contrary to similar eliminations by DBU of benzoic acid from benzoylated glycosyl cyanides[18,19], as well as of acetic acid from acetylated β-D-mannopyranosyl cyanide[20]. Thin layer chromatography (TLC) of the reaction mixtures indicated the presence of several polar compounds which were thought to be partially or fully deacetylated products, since DBU had been reported to bring about deacetylation even in aprotic solvents[21]. Trials to improve the yields of 1-cyanoglycals by reacetylation of the mixtures with pyridine–acetic anhydride failed and, therefore, the starting materials were prepared by a bromination[22]–



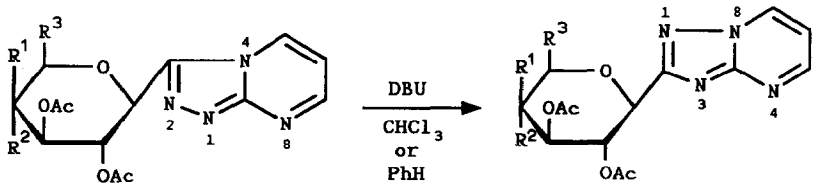
1-4 5-7 8-10 11-14 19

	R^1	R^2	R^3
1, 5, 8, 11, 15	OAc	H	CH_2OAc
15a	OH	H	CH_2OH
2, 12, 16	H	OAc	CH_2OAc
16a	H	OH	CH_2OH
3, 6, 9, 13, 17	OAc	H	H
17a	OH	H	H
4, 7, 10, 14, 18	H	OAc	H
18a	H	OH	H

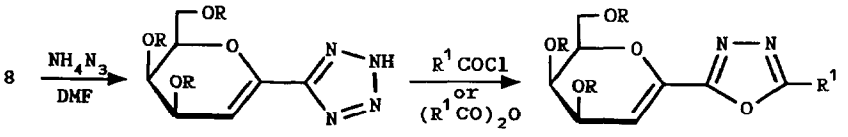
Scheme 1.

elimination[16] sequence (e.g., **1** → **5** → **8**) in overall yields of ~60% for the two steps (Scheme 1).

Heterocyclisation of the cyano group in **8** was first tried with 2-aminothiophenol, according to previously described transformations[23–27], to give the corresponding



	R^1	R^2	R^3	
20	OAc	H	CH_2OAc	21
22	H	OAc	H	23



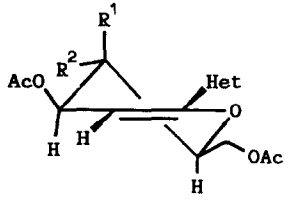
		R^1	CH_3	CF_3	CH_2Cl	CO_2Et	$CONH_2$
24	R = Ac	R = Ac	25	26	27	28	
24a	R = H	R = H	25a		27a		28a

Scheme 2.

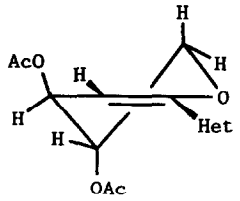
benzothiazole **15** in 32% yield. Applying the zinc–pyridine method[16] to the known 2-(1-bromo-D-galactopyranosyl)benzothiazole[22] **19** produced **15** in 38% yield. Interestingly, DBU in chloroform eliminated acetic acid from the acetylated 2-(β-D-galactopyranosyl)benzothiazole[23] **11** without side-reactions, and **15** was obtained in 77% yield. The analogous compounds **16–18** were prepared by this reaction in 47–57% yields, respectively.

To investigate the influence of DBU on another system, its reaction with 3-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-[1,2,4]triazolo[4,3-*a*]pyrimidine[28] (**20**) and its xylopyranosyl analogue[28] **22** was studied under similar conditions. This reaction (Scheme 2) led to the [1,5-*a*] ring isomers **21** and **23**, respectively, instead of the expected 1′-enopyranosyl derivatives. This Dimroth-like rearrangement is characteristic of the 3-glycosyl-[1,2,4]triazolo[4,3-*a*]pyrimidines and similar ring-fused [1,2,4]triazolo systems[29–32]. The ^{13}C NMR spectra allow unambigous assignments of the isomeric compounds[31–33]. Being attached to two sp^2-hybridised nitrogens, the C-2 atoms in **21** and **23** resonate at lower fields as compared to the C-3 atoms in **20** and **22** having one sp^2- and one sp^3-hybridized neighbouring nitrogens.

Transformation of **8**, with ammonium azide in *N*,*N*-dimethylformamide (DMF) under previously described conditions[23–27], into the corresponding tetrazole **24** was



$^4H_5$



$^5H_4$

	R^1	R^2
15, 24, 25–28	OAc	H
16	H	OAc

18

Scheme 3.

achieved in 57% yield. No product of a 1,4-addition of azide onto the α,β-unsaturated nitrile could be isolated from these reactions.

Tetrazole **24** was transformed[23–27] by various acylating agents into the 2,5-disubstituted-1,3,4-oxadiazoles **25–28**. Attempts to reduce the number of steps required for the preparation of **25** by elimination of acetic acid with DBU from the corresponding acetylated 2-(β-D-galactopyranosyl)-5-methyl-1,3,4-oxadiazole[24] resulted in complex mixtures from which no discrete products could be isolated.

The *C*-(1-enopyranosyl)heterocycles exhibited first-order analysable ^{1}H NMR spectra. Evaluating the coupling constants for the D-*lyxo* compounds **15, 24** and **25–28** ($^4J_{2',4'}$ 1.2–1.6, $^4J_{3',5'}$ 1–1.3 Hz) suggested that H-2′ and H-4′ as well as H-3′ and H-5′ are nearly coplanar in these compounds which therefore exist mainly as the $^4H_5$ conformers (Scheme 3). For the D-*arabino* compound **16**, the $^3J_{3',4'}$ 5 and $^3J_{4',5'}$ 6 Hz couplings also suggested $^4H_5$ as the dominating conformer. For **18**, long-range couplings could again be observed ($^4J_{2',4'}$ 1.2, $^4J_{3',5'}$ 1.7 Hz) which, because of the D-*threo* configuration, indicated a preponderating $^5H_4$ conformer for this compound. These observations are in accord with those for glycals[34–36], 1-cyanoglycals[16,37], and related compounds[9], and suggest that substitution at C-1 has no significant influence on the conformation of the 1-enopyranosyl moiety.

Each of the prepared C-(2-deoxyhex/pent-1-enopyranosyl)heterocycles **15–18, 24, 25**, and **27** was deacetylated by the Zemplén method to give **15a–18a, 24a, 25a**, and **27a**, while **28** was deprotected with methanolic ammonia to obtain **28a**. Compound **26** did not give an isolable deprotected product under several deacetylation conditions.

It can be concluded from this work that a general method for the synthesis of *C*-(2-deoxyhex/pent-1-enopyranosyl) compounds does not exist. The results of the tempting and straightforward base-induced elimination of acid from the fully acylated *C*-glycosyl derivatives depend clearly not only on the nature of the aglycon but also on that of the acyl protecting groups applied as well as on the sugar

configuration (cf. also refs 9, 14, and 18–20). Therefore, a careful selection of base and reaction conditions, use of other reaction sequences (e.g., bromination[22]-elimination[16]), or other approaches based on entirely different reactions[6,7] cannot be avoided.

EXPERIMENTAL

General methods.—Melting points were measured in open capillary tubes or on a Kofler hot-stage and are uncorrected. Optical rotations were determined with a Perkin–Elmer 241 polarimeter at room temperature. NMR spectra were recorded with a Bruker WP 200 SY spectrometer (^{1}H, 200 MHz; ^{13}C, 50.3 MHz), for $CDCl_3$ solutions with internal Me_4Si unless otherwise stated. TLC was performed on DC-Alurolle, Kieselgel 60 F_{254} (Merck), and column chromatography on Kieselgel 60 (Merck). TLC plates were visualised by gentle heating. Organic solutions were dried over anhyd $MgSO_4$ and concentrated in vacuo at 40–50°C (water bath). Deprotection of the acetylated compounds was performed by the Zemplén method[38] unless otherwise stated.

(1R)-2,3,4-Tri-O-acetyl-1-bromo-L-arabinopyranosyl cyanide (**6**).—A mixture of 2,3,4-tri-*O*-acetyl-α-L-arabinopyranosyl cyanide[39] (**3**; 0.286 g, 1 mmol), *N*-bromosuccinimide (0.196 g, 1.1 mmol), and benzoyl peroxide (0.04 g, 0.17 mmol) was refluxed in CCl_4 (8 mL) for 40 min. After cooling, the mixture was filtered and the filtrate was washed with satd aq $NaHCO_3$, dried, and evaporated to dryness. The residue afforded, after crystallisation from EtOH, **6** (0.284 g, 78%); mp 102–103°C; $[\alpha]_D$ +248° (*c* 0.6, $CHCl_3$). The D enantiomer has mp 103–104°C and $[\alpha]_D$ −250° ($CHCl_3$)[22]. Both enantiomers have identical ^{1}H and ^{13}C NMR spectra. Anal. Calcd for $C_{12}H_{14}BrNO_7$ (364.16): C, 39.57; H, 3.87; N, 3.84; Br, 21.94. Found: C, 39.77; H, 3.81; N, 3.77; Br, 21.89.

4,5,7-Tri-O-acetyl-2,6-anhydro-3-deoxy-D-lyxo-hept-2-enononitrile (**8**).—2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl cyanide[17,40] (**1**; 1.0 g, 3.34 mmol) was dissolved in dry $CHCl_3$ (30 mL) and then DBU (0.75 mL, 5 mmol) was added. The mixture was left at room temperature for 24 h, then washed with satd aq $KHSO_4$, and dried, and the solvent was evaporated. The residual syrup crystallised from abs EtOH to give **8** (0.34 g, 40%); mp 115–116°C; $[\alpha]_D$ −52° (*c* 1.2, $CHCl_3$); lit.[16]: mp 113–115°C; $[\alpha]_D$ −52° ($CHCl_3$).

4,5-Di-O-acetyl-2,6-anhydro-3-deoxy-L-erythro-hex-2-enononitrile (**9**).—*(a) From the bromo compound* **6**. Compound **6** (1 g, 2.75 mmol) was dissolved in dry benzene (15 mL) and Zn dust (0.3 g) was added. The mixture was stirred and heated to reflux. Pyridine (0.22 mL, 2.75 mmol) was added to the mixture and boiling was continued for 40 min. After cooling to 20°C, the solids were filtered off, and the filtrate was washed with satd aq $KHSO_4$, dried, and evaporated to dryness. The residue crystallised from EtOH to give **9** (0.46 g, 72%); mp 89–90°C; $[\alpha]_D$ −200° (*c* 1.1, $CHCl_3$); ^{1}H NMR (C_6D_6): δ 5.12 (ddd, 1 H, $J_{4,5}$ 4.1, $J_{4,6e}$ 1.5 Hz, H-4), 4.92

(dd, 1 H, $J_{3,4}$ 4, $J_{3,5}$ 0.9 Hz, H-3), 4.82 (dddd, 1 H, $J_{5,6a}$ 2.7 Hz, H-5), 3.45 (dd, 1 H, $J_{5,6e}$ 6.9, H-6*e*), 3.15 (ddd, 1 H, $J_{6e,6a}$ 10.3 Hz, H-6*a*), 1.60, 1.50 (2 s, 6 H, 2 Ac); ^{13}C NMR: δ 169.76, 169.62 (C=O), 131.93 (C-2), 113.09 (CN), 111.75 (C-3), 65.37 (C-6), 63.60, 62.06 (C-4,5), 20.51 (CH_3). Anal. Calcd for $C_{10}H_{11}NO_5$ (225.2): C, 53.33; H, 4.92; N, 6.22. Found: C, 53.47; H, 4.76; N, 6.24.

(b) From cyanide **3** *with DBU.* Compound **3**[39] (1.0 g, 3.5 mmol), prepared from 2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl bromide and mercury(II) cyanide according to the general procedure of ref 17, was dissolved in dry CH_2Cl_2 (30 mL) and DBU (0.52 mL, 3.5 mmol) was added. The mixture was stirred at room temperature for 24 h, then washed with satd aq $KHSO_4$, dried, and evaporated to dryness. The residue crystallised from EtOH to give **9** (0.41 g, 51%); mp 88–89°C; $[\alpha]_D$ −199° (*c* 1.0, $CHCl_3$).

*4,5-Di-*O*-acetyl-2,6-anhydro-3-deoxy-*D-threo*-hex-2-enononitrile* (**10**).—A solution of 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl cyanide[17,41] (**4**; 2.0 g, 7 mmol) and DBU (1 mL, 7 mmol) in CH_2Cl_2 (100 mL) was left at room temperature for 48 h, and then evaporated to dryness. The residue was triturated with water (100 mL) and extracted with diethyl ether (3 × 100 mL). The dried organic phases were evaporated and the residue was chromatographed on silica gel with 8:2 hexane–EtOAc to give **10** (0.8 g, 51%) as a syrup; $[\alpha]_D$ −277° (*c* 1.2, $CHCl_3$); lit.[16]: $[\alpha]_D$ −274° ($CHCl_3$); ^{1}H NMR (C_6D_6): δ 5.40 (dd, 1 H, $J_{3,4}$ 5, $J_{3,5}$ 1.5 Hz, H-3), 4.83 (ddd, 1 H, $J_{4,5}$ 5, $J_{4,6a}$ 0.5 Hz, H-4), 4.67 (m, 1 H, H-5), 3.81 (ddd, 1 H, $J_{4,6e}$ ~ 1.8, $J_{5,6e}$ 3 Hz, H-6*e*), 3.41 (dd, 1 H, $J_{5,6a}$ 1.5, $J_{6e,6a}$ 12.5 Hz, H-6*a*), 1.58, 1.52 (2 s, 6 H, 2 Ac); ^{13}C NMR: δ 169.78, 169.13 (C=O), 132.97 (C-2), 113.83 (CN), 110.89 (C-3), 65.98 (C-6), 65.22, 65.20 (C-4,5), 20.20, 20.11 (CH_3). Anal. Calcd for $C_{10}H_{11}NO_5$ (225.2): C, 53.35; H, 4.92; N, 6.22. Found: C, 53.60; H, 4.89; N, 6.04.

*2-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)benzothiazole* (**12**).—A solution of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl cyanide[17] (**2**; 1.8 g, 5 mmol) and 2-aminothiophenol (1.1 mL, 10 mmol) in anhyd EtOH (35 mL) was boiled for 4 h under N_2. The mixture was cooled, and the product was collected and recrystallised from EtOH to yield **12** (1.81 g, 77%); mp 129–130°C; $[\alpha]_D$ − 20° (*c* 1.3, $CHCl_3$); ^{1}H NMR: δ 7.94 (m, 2 H, aryl), 7.41 (m, 2 H, aryl), 5.44 (dd, 1 H, $J_{3',4'}$ 9 Hz, H-3'), 5.31 (dd, 1 H, $J_{4',5'}$ 4.5 Hz, H-4'), 5.24 (dd, 1 H, $J_{2',3'}$ 9 Hz, H-2'), 4.93 (d, 1 H, $J_{1',2'}$ 9.2 Hz, H-1'), 4.35 (dd, 1 H, $J_{6'a,6'b}$ 11.2 Hz, H-6'a), 4.24 (dd, 1 H, $J_{5',6'b}$ 10 Hz, H-6'b), 3.96 (m, 1 H, $J_{5',6'a}$ 2.5 Hz, H-5'), 2.15, 2.10, 2.05, 1.96 (4 s, 12 H, 4 Ac); ^{13}C NMR: δ 170.34, 169.92, 169.20, 169.02 (C=O), 166.30 (C-2), 152.42 (C-3a), 134.68 (C-7a), 125.99, 125.37, 123.10, 121.70 (C-4,5,6,7), 77.30, 76.20, 73.40, 71.20, 68.20 (C-1',2',3',4',5'), 61.76 (C-6'), 20.51, 20.38 (CH_3). Anal. Calcd for $C_{21}H_{23}NO_9S$ (465.5): C, 54.18; H, 4.98; N, 3.01; S, 6.81. Found: C, 53.87; H, 4.89; N, 3.08; S, 6.71.

*2-(2,3,4-Tri-*O*-acetyl-α-L-arabinopyranosyl)benzothiazole* (**13**).—A solution of 2,3,4-tri-*O*-acetyl-α-L-arabinopyranosyl cyanide[39] (**3**; 4 g, 14 mmol) and 2-aminothiphenol (3.1 mL, 28 mmol) in anhyd EtOH was boiled for 6.5 h under N_2. The mixture was cooled and the product was collected and recrystallized from

EtOH to give **13** (4.1 g, 74%); mp 159–160°C; $[\alpha]_D$ +11° (*c* 1.1, $CHCl_3$); ^1H NMR: δ 7.95 (m, 2 H, aryl), 7.45 (m, 2 H, aryl), 5.56 (dd, 1 H, $J_{2',3'}$ 10 Hz, H-2'), 5.46 (ddd, 1 H, $J_{4',5'a}$ 2.5 Hz, H-4'), 5.25 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, H-3'), 4.83 (d, 1 H, $J_{1',2'}$ 9.8 Hz, H-1'), 4.24 (dd, 1 H, $J_{4',5'a}$ 2.5 Hz, H-5'a), 3.92 (dd, 1 H, $J_{5'a,5'b}$ 13 Hz, H-5'b), 2.22, 2.02, 2.01 (3 s, 9 H, 3 Ac); ^{13}C NMR: δ 169.70, 169.30, 169.12 (C=O), 167.04 (C-2), 152.38 (C-3a), 134.55 (C-7a), 125.86, 125.16, 122.94, 121.58 (C-4,5,6,7), 77.99, 70.81, 68.70, 68.05, 67.57 (C-1',2',3',4',5'), 20.59, 20.32, 20.06 (CH_3). Anal. Calcd for $C_{18}H_{19}NO_7S$ (393.4): C, 54.95; H, 4.86; N, 3.56; S, 8.15. Found: C, 55.12; H, 4.81; N, 3.59; S, 8.12.

*2-(Per-*O*-acetyl-2-deoxy-1-enopyranosyl)benzothiazoles* (**15–18**).—*General procedure.* To a solution of **11–14** (1 mmol) in $CHCl_3$ (15 mL) was added dropwise DBU (0.75 mL, 5 mmol). The solution was heated on a water bath until the starting material disappeared (3–4 h; TLC, 4:6 benzene–ether). The cold mixture was then washed with satd aq $KHSO_4$, dried, and evaporated to dryness, and the residual syrup was crystallised from EtOH.

*2-(3,4,6-Tri-*O*-acetyl-2-deoxy-*D*-lyxo-hex-1-enopyranosyl)benzothiazole* (**15**).—*(a) By the general procedure.* Yield: 77%; mp 87–88°C; $[\alpha]_D$ −66° (*c* 1.2, $CHCl_3$); ^1H NMR: δ 8.04, 7.91 (2 dd, each 1 H, H-4,7), 7.51, 7.41 (2 dt, each 1 H, H-5,6), 6.05 (dd, 1 H, $J_{2',3'}$ 3, $J_{2',4'}$, 1.5 Hz, H-2'), 5.81 (ddd, 1 H, $J_{3',4'}$ 4.7, $J_{3',5'}$, 1 Hz, H-3'), 5.57 (dt, 1 H, $J_{4',5'}$ 1.5 Hz, H-4'), 4.62 (m, 1 H, H-5'), 4.49 (dd, 1 H, $J_{5',6'a}$ 7 Hz, H-6'a), 4.33 (dd, 1 H, $J_{5'6'b}$ 5.5 Hz, $J_{6'a,6'b}$ 11.5 Hz, H-6'b), 21.5, 2.13, 2.07 (3 s, 9 H, 3 Ac); ^{13}C NMR: δ 170.37, 170.06 (C=O), 161.90 (C-2), 153.3 (C-1'), 147.92 (C-3a), 134.91 (C-7a), 126.42, 125.54, 123.49, 121.64 (C-4,5,6,7), 99.61 (C-2'), 74.22, 64.56, 63.13 (C-3',4',5'), 61.35 (C-6'), 20.64, 20.53 (CH_3). Anal. Calcd for $C_{19}H_{19}NO_7S$ (405.4): N, 3.45; S, 7.91. Found: N, 3.30; S, 7.75.

(b) From the cyanogalactal **8**. A solution of **8** (0.5 g, 1.68 mmol) and 2-aminothiophenol (0.2 mL, 1.78 mmol) in abs EtOH (5 mL) was boiled for 5 h under N_2. The mixture was cooled, then the crystalline product was collected and recrystallised from abs EtOH to give **15** (0.218 g 32%); mp 85–86°C; $[\alpha]_D$ −67° (*c* 1.0, $CHCl_3$).

(c) From the 2-(1-bromogalactosyl)benzothiazole **19**. Compound **19**[22] (0.544 g, 1 mmol) was dissolved in dry benzene (15 mL) and Zn dust (0.3 g) was added. The mixture was stirred and heated to reflux. After addition of pyridine (0.08 mL, 1 mmol) to the hot suspension and boiling for 10 min, the starting material disappeared (TLC, 1:1 benzene–ether). The mixture was cooled and filtered, and the filtrate was washed with satd aq $KHSO_4$, dried, decolourised with charcoal, and evaporated to dryness. The residual syrup crystallised from abs EtOH to give **15** (0.154 g, 38%); mp 86–87°C; $[\alpha]_D$ −66° (*c* 1.3, $CHCl_3$).

*2-(2-Deoxy-*D*-lyxo-hex-1-enopyranosyl)benzothiazole* (**15a**).—Yield: 90%; mp 234–235°C (from EtOH); $[\alpha]_D$ −53° (*c* 1.4, Me_2SO); ^1H NMR (pyridine-d_5): δ 8.14, 7.90 (2 dd, each 1 H, H-4,7), 7.46, 7.32 (2 t, each 1 H, H-5,6), 7.1–6.7 (br s, 3 H, 3 OH), 6.63 (br s, 1 H, H-2'), 5.0 (br s, 1 H, H-3'), 4.68–4.60 (m, 4 H, H-4',5', 6'a,6'b); ^{13}C NMR (Me_2SO-d_6): δ 158.20 (C-2), 152.95 (C-1'), 143.30 (C-3a),

132.10 (C-7a), 126.46, 125.22, 122.73, 122.31 (C-4,5,6,7), 105.88 (C-2), 79.19, 64.35, 63.72 (C-3',4',5'), 60.06 (C-6'). Anal. Calcd for $C_{13}H_{13}NO_4S$ (279.3): N, 5.01; S, 11.48. Found: N, 4.86; S, 11.22.

2-(3,4,6-Tri-O-*acetyl-2-deoxy*-D-arabino-*hex-1-enopyranosyl)benzothiazole* (**16**).—Yield: 47%; mp 117–118°C; $[\alpha]_D$ −76° (*c* 1.4, $CHCl_3$); ^1H NMR: δ 8.05, 7.91 (2 dd, each 1 H, H-4,7), 7.51, 7.41 (2 dt, each 1 H, H-5,6), 6.19 (d, 1 H, $J_{2',3'}$ 4 Hz, H-2'), 5.57 (dd, 1 H, $J_{3',4'}$ 5 Hz, H-3'), 5.35 (dd, 1 H, $J_{4',5'}$ 6 Hz, H-4'), 4.61 (m, 2 H, H-6'a,6'b), 4.32 (m, 1 H, H-5'), 2.14, 2.10, 2.09 (3 s, 9 H, 3 Ac); ^{13}C NMR: δ 170.45, 170.06, 169.47 (C=O), 162.30 (C-2), 153.37 (C-1'), 148.07 (C-3a), 135.03 (C-7a), 126.49, 125.66, 123.60, 121.66 (C-4,5,6,7), 99.12 (C-2'), 75.20, 67.12, 67.01 (C-3',4',5'), 60.81 (C-6'), 20.81, 20.67 (CH_3). Anal. Calcd for $C_{19}H_{19}NO_7S$ (405.4): N, 3.45; S, 7.91. Found: N, 3.34; S, 7.80.

2-(2-Deoxy-D-arabino-*hex-1-enopyranosyl)benzothiazole* (**16a**).—Yield: 80%; mp 220–221°C (from EtOH); $[\alpha]_D$ +23° (*c* 1.4, Me_2SO); ^1H NMR (Me_2SO-d_6): δ 8.08 (m, 2 H, aryl), 7.50 (m, 2 H, aryl), 5.94 (d, 1 H, $J_{2',3'}$ 3 Hz, H-2'), 4.17 (dd, 1 H, $J_{3',4'}$ 6.6 Hz, H-3'), 3.96 (ddd, 1 H, $J_{5',6'a}$ 2.5 Hz, H-5'), 3.85 (dd, 1 H, $J_{6'a,6'b}$ 12.4 Hz, H-6'a), 3.73 (dd, 1 H, $J_{5',6'b}$ 5 Hz, H-6'b), 3.8–3.6 (br s, 3 H, 3 OH), 3.57 (m, 1 H, $J_{4',5'}$ 9 Hz, H-4); ^{13}C NMR (Me_2SO-d_6): δ 160.30 (C-2), 154.74 (C-1'), 145.38 (C-3a), 134.47 (C-7a), 126.80, 125.54, 122.91, 122.50 (C-4,5,6,7), 105.84 (C-2'), 81.13, 68.63, 67.50 (C-3',4',5'), 60.14 (C-6'). Anal. Calcd for $C_{13}H_{13}NO_4S$ (279.3): N, 5.01; S, 11.48. Found: N, 4.77; S, 11.10.

2-(3,4-Di-O-*acetyl-2-deoxy*-L-erythro-*pent-1-enopyranosyl)benzothiazole* (**17**).—Yield: 53%; mp 132–133°C; $[\alpha]_D$ −1° (*c* 2.3, $CHCl_3$); ^1H NMR: δ 8.05, 7.90 (2 dd, each 1 H, H-4,7), 7.50, 7.40 (2 dt, each 1 H, H-5,6), 6.12 (d, 1 H, $J_{2',3'}$ 4.8 Hz, H-2'), 5.72 (dd, 1 H, $J_{3',4'}$ 4.8 Hz, H-3'), 5.37 (m, 1 H, H-4'), 4.35, 4.32 (2 s, 2 H, H-5'*e*,5'*a*), 2.22, 2.21 (2 s, 6 H, 2 Ac); ^{13}C NMR: δ 169.97, 169.91 (C=O), 161.87 (C-2), 153.22 (C-1'), 149.58 (C-3a), 134.85 (C-7a), 126.32, 125.54, 123.50, 121.53 (C-4,5,6,7), 98.60 (C-2'), 65.04, 64.48, 63.02 (C-3',4',5'), 20.67, 20.53 (CH_3). Anal. Calcd for $C_{16}H_{15}NO_5S$ (333.3): N, 4.20; S, 9.62. Found: N, 3.96; S, 9.36.

2-(2-Deoxy-L-erythro-*pent-1-enopyranosyl)benzothiazole* (**17a**).—Yield: 84%; mp 182–183°C (from EtOH); $[\alpha]_D$ +4° (*c* 1.2, Me_2SO); ^1H NMR (Me_2SO-d_6): δ 8.07, 7.97 (2 dd, each 1 H, H-4, 7), 7.50, 7.42 (2 dd, each 1 H, H-5,6), 6.01 (d, 1 H, $J_{2',3'}$ 5 Hz, H-2'), 4.25 (dd, 1 H, $J_{3',4'}$ 5 Hz, H-3'), 4.14–3.99 (m, 2 H, H-5'a,b), 3.85–3.70 (m, 1 H, H-4'), 3.60 (br s, 2 H, 2 OH); ^{13}C NMR (Me_2SO-d_6): δ 163.05 (C-2), 152.93 (C-1'), 146.23 (C-3a), 134.20 (C-7a), 126.46, 125.31, 122.80, 122.23 (C-4,5,6,7), 104.34 (C-2'), 66.90, 64.97, 61.77 (C-3',4',5'). Anal. Calcd for $C_{12}H_{11}NO_3S$ (249.2): N, 5.62; S, 12.86. Found: N, 5.60; S, 12.52.

2-(3,4-Di-O-*acetyl-2-deoxy*-D-threo-*pent-1-enopyranosyl)benzothiazole* (**18**).—Yield: 57%; mp 107–108°C; $[\alpha]_D$ +192° (*c* 1.2, $CHCl_3$); ^1H NMR: δ 8.06, 7.91 (2 dd, each 1 H, H-4, 7), 7.50, 7.41 (2 dt, each 1 H, H-5,6), 6.25 (dd, 1 H, $J_{2',3'}$ 5.3, $J_{2',4'}$ 1.2 Hz, H-2'), 5.28 (dd, 1 H, $J_{3',4'}$ 2.8, $J_{3',5'e}$ 1.7 Hz, H-3'), 5.09 (m, 1 H, H-4'), 4.53 (ddd, 1 H, $J_{4',5'e}$ 3.1 Hz, H-5'*e*), 4.26 (dd, 1 H, $J_{4',5'a}$ 1.2, $J_{5'e,5'a}$ 12.2 Hz, H-5'*a*), 2.10, 2.09 (2 s, 6 H, 2 Ac); ^{13}C NMR: δ 169.81, 169.50 (C=O), 162.43

(C-2), 153.04 (C-1'), 150.04 (C-3a), 134.88 (C-7a), 126.45, 125.67, 123.66, 121.62 (C-4,5,6,7), 98.24 (C-2'), 66.86, 65.04, 63.86 (C-3',4',5'), 20.92, 20.83 (CH_3). Anal. Calcd for $C_{16}H_{15}NO_5S$ (333.3): N, 4.20; S, 9.62. Found: N, 4.14; S, 9.50.

*2-(2-Deoxy-*D-threo-*pent-1-enopyranosyl)benzothiazole* (**18a**).—Yield: 65%; mp 159–160°C (from EtOH); $[\alpha]_D$ −25° (*c* 1.0, MeOH); ^{1}H NMR (Me_2SO-d_6): δ 8.12, 8.04 (2 d, each 1 H, H-4, 7), 7.54, 7.43 (2 t, each 1 H, H-5,6), 6.07 (d, 1 H, $J_{2',3'}$ 4.5 Hz, H-2'), 4.15 (m, 2 H, H-5'a,5'b), 3.94 (dd, 1 H, $J_{3',4'}$ ~ 4.5 Hz, H-3'), 3.68 (m, 1 H, H-4'), 3.67–3.25 (2 H, 2 OH); ^{13}C NMR (Me_2SO-d_6): δ 162.90 (C-2), 152.95 (C-1'), 146.21 (C-7a), 134.17 (C-3a), 126.56, 125.39, 122.85, 122.36 (C-4,5,6,7), 103.83 (C-2'), 67.54, 67.28, 60.90 (C-3',4',5'). Anal. Calcd for $C_{12}H_{11}NO_3S$ (249.2): N, 5.62; S, 12.86. Found: N, 5.30; S, 12.50.

*3-(2,3,4,6-Tetra-*O-*acetyl-β-*D-*galactopyranosyl)-[1,2,4]triazolo[4,3-*a*]-pyrimidine*[28] (**20**).—A solution of 5-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)tetrazole[23] (4.00 g, 10 mmol) and 2-chloropyrimidine (1.72 g, 15 mmol) in dry toluene (35 mL) was refluxed for 30 h and then evaporated to dryness. The residue was dissolved in $CHCl_3$, the solution was washed with satd aq $NaHCO_3$, and the dried organic phase was evaporated. The residue was then crystallised from a mixture of EtOH–ether–acetone to yield **20** (2.56 g, 57%); mp 163–164°C; $[\alpha]_D$ −56° (*c* 1.4, $CHCl_3$); ^{1}H NMR: δ 8.74 (dd, 1 H, H-7), 8.71 (dd, 1 H, H-5), 7.01 (dd, 1 H, H-6), 5.65 (d, 1 H, $J_{4',5'}$ ~ 0 Hz, H-4'), 5.52 (dd, 1 H, $J_{2',3'}$ 10.1 Hz, H-2'), 5.32 (dd, 1 H, $J_{3',4'}$ 3.4 Hz, H-3'), 5.19 (d, 1 H, $J_{1',2'}$ 10.3 Hz, H-1'), 4.21 (s, 3 H, H-5',6'a,6'b), 2.27, 2.26, 2.01, 1.89 (4 s, 12 H, 4 Ac); ^{13}C NMR: δ 170.33, 169.77, 169.21 (C=O), 154.58 (C-3), 151.10 (C-8a), 140.91 (C-7), 132.15 (C-5), 110.06 (C-6), 75.38, 74.31, 70.91, 67.68, 65.86 (C-1',2',3',4',5'), 61.47 (C-6'), 20.63, 20.56, 20.46, 20.24 (CH_3). Anal. Calcd for $C_{19}H_{22}N_4O_9$ (450.4): C, 50.66; H, 4.92; N, 12.44. Found: C, 50.53; H, 4.97; N, 12.57.

*2-(2,3,4,6-Tetra-*O-*acetyl-β-*D-*galactopyranosyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine* (**21**).—A solution of **20** (0.45 g, 1 mmol) and DBU (0.15 mL, 1 mmol) in dry $CHCl_3$ (10 mL) was stirred at room temperature for 24 h, and then diluted with $CHCl_3$. The solution was washed with satd aq $KHSO_4$. The dried organic phase was evaporated and the residue was chromatographed on silica gel with 97:3 $CHCl_3$–MeOH to give **21** (0.135 g, 30%) as a syrup; $[\alpha]_D$ −68° (*c* 1.5, $CHCl_3$); ^{1}H NMR: δ 8.91 (dd, 1 H, H-7), 8.86 (dd, 1 H, H-5), 7.19 (dd, 1 H, H-6), 5.76 (dd, 1 H, $J_{2',3'}$ 10 Hz, H-2'), 5.58 (d, 1 H, $J_{4',5'}$ ~ 0 Hz, H-4'), 5.28 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, H-3'), 4.90 (d, 1 H, $J_{1',2'}$ 10 Hz, H-1'), 4.3–4.1 (m, 3 H, H-5',6'a,6'b), 2.21, 2.05, 2.02, 1.92 (4 s, 12 H, 4 Ac); ^{13}C NMR: δ 170.28, 169.23 (C=O), 164.37 (C-2), 159.70 (C-3a), 154.98 (C-7), 136.02 (C-5), 110.58 (C-6), 75.18, 75.18, 71.97, 68.19, 64.44 (C-1',2',3',4',5'), 61.64 (C-6'), 20.57 (CH_3). Anal. Calcd for $C_{19}H_{22}N_4O_9$ (450.4): C, 50.66; H, 4.92; N, 12.44. Found: C, 50.71; H, 4.87; N, 12.62.

*3-(2,3,4-Tri-*O-*acetyl-β-*D-*xylopyranosyl)-[1,2,4]triazolo[4,3-*a*]pyrimidine*[28] (**22**).—A solution of 5-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)tetrazole[23] (1.97 g, 6 mmol) and 2-chloropyrimidine (1.03 g, 9 mmol) in dry toluene (15 mL) was refluxed for 30 h. Work-up as described for **20** gave **22** (1.21 g, 53%); mp 208–209°C (from EtOH);

$[\alpha]_D$ −149° (*c* 1.3, $CHCl_3$); ^1H NMR: δ 8.69 (m, 2 H, H-5,7), 6.98 (dd, 1 H, H-6), 5.42 (dd, 1 H, $J_{3',4'}$ 9 Hz, H-3'), 5.31 (dd, 1 H, $J_{2',3'}$ 9 Hz, H-2'), 5.20 (m, 1 H, $J_{4',5'e}$ 5.5. Hz, H-4'), 5.09 (d, 1 H, $J_{1',2'}$ 9.8 Hz, H-1'), 4.43 (dd, 1 H, $J_{4',5'a}$ 11.5 Hz, H-5'*a*), 3.59 (dd, 1 H, $J_{5'e,5'a}$ 11 Hz, H-5'*e*), 2.10, 2.08, 1.85 (3 s, 9 H, 3 Ac); ^{13}C NMR: δ 170.91, 170.79, 170.40 (C=O), 157.02 (C-3), 155.83 (C-8a), 142.90 (C-7), 135.41 (C-5), 111.66 (C-6), 74.42, 73.94, 70.54, 70.22, 67.96 (C-1',2',3',4',5'), 21.91, 21.83, 21.67 (CH_3). Anal. Calcd for $C_{16}H_{18}N_4O_7$ (378.3): C, 50.80; H, 4.79; N, 14.81. Found: C, 50.62; H, 4.71; N, 14.50.

*2-(2,3,4-Tri-*O*-acetyl-β-*D*-xylopyranosyl)-[1,2,4]triazolo[1,5-*a*]pyrimidine* (**23**).—A solution of **22** (0.378 g, 1 mmol) and DBU (0.15 mL, 1 mmol) in dry benzene (10 mL) was heated on a water bath for 18 h and then evaporated to dryness. The residue was crystallised from EtOH to give **23** (0.302 g, 80%); mp 214–216°C; $[\alpha]_D$ −44° (*c* 1.1, $CHCl_3$); ^1H NMR: δ 8.85 (d, 2 H, H-5,7), 7.15 (t, 1 H, H-6), 5.49 (dd, 1 H, $J_{3',4'}$ 9 Hz, H-3'), 5.41 (dd, 1 H, $J_{2',3'}$ 9 Hz, H-2'), 5.20 (m, 1 H, $J_{4',5'e}$ 5.5 Hz, H-4'), 4.82 (d, 1 H, $J_{1',2'}$ 9.2 Hz, H-1'), 4.36 (dd, 1 H, $J_{4',5'a}$ 10.8 Hz, H-5'*a*), 3.56 (dd, 1 H, $J_{5'e,5'a}$ 11.3 Hz, H-5'*e*), 2.08, 2.06, 1.94 (3 s, 9 H, 3 Ac); ^{13}C NMR: δ 170.0, 169.61 (C=O), 164.58 (C-2), 159.0 (C-3a), 155.0 (C-7), 135.97 (C-5), 110.61 (C-6), 74.97, 73.34, 70.99, 68.82, 67.18 (C-1',2',3',4',5'), 20.56 (CH_3). Anal. Calcd for $C_{16}H_{18}N_4O_7$ (378.3): C, 50.80; H, 4.79; N, 14.81. Found: C, 50.75; H, 4.77; N, 14.80.

*5-(3,4,6-Tri-*O*-acetyl-2-deoxy-*D*-lyxo-hex-1-enopyranosyl)tetrazole* (**24**).—A mixture of the unsaturated nitrile **8** (10 g, 33.63 mmol), NaN_3 (4.37 g, 67.26 mmol), and NH_4Cl (3.60 g, 67.26 mmol) in *N,N*-dimethylformamide (50 mL) was heated on a hot water bath for 3.5 h. After cooling to room temperature, the mixture was filtered and the filtrate was evaporated to dryness. The residual oil was treated with a cold mixture of Ac_2O (10 mL) and pyridine (5 mL). After standing at room temperature for 16 h, the solution was concentrated and the oily residue was triturated with ice-cold water. Chloroform (250 mL) was added and the mixture was partitioned between water and $CHCl_3$. The aqueous phase was washed with $CHCl_3$ (2 × 50 mL). The combined organic phases were washed with satd aq $NaHCO_3$ (3 × 100 mL). These last aq phases were acidified with 5 M HCl, then extracted with $CHCl_3$ (3 × 50 mL). The combined organic phases were dried and evaporated. The oily residue was crystallised from water to yield **24** (6.52 g, 57%); mp 174–177°C; $[\alpha]_D$ −53° (*c* 1.2, pyridine); ^1H NMR: δ 8.2–7.8 (br s, 1 H, NH), 6.12 (dd, 1 H, $J_{2',3'}$ 2.7, $J_{2',4'}$ 1.5 Hz, H-2'), 5.79 (ddd, 1 H, $J_{3',4'}$ 4.5, $J_{3',5'}$ 1 Hz, H-3'), 5.59 (ddd, 1 H, $J_{4',5'}$ 1.5 Hz, H-4'), 4.60 (m, 1 H, $J_{5',6'b}$ 5 Hz, H-5'), 4.50 (dd, 1 H, $J_{5',6'a}$ 7 Hz, H-6'a), 4.30 (dd, 1 H, $J_{6'a,6'b}$ 11.5 Hz, H-6'b), 2.15, 2.14, 2.08 (3 s, 9 H, 3 Ac); ^{13}C NMR: δ 170.05, 169.68 (C=O), 151.50 (C-5), 141.57 (C-1'), 101.80 (C-2'), 73.73, 63.89, 62.52 (C-3',4',5'), 60.94 (C-6'), 20.34, 20.29, 20.20 (CH_3). Anal. Calcd for $C_{13}H_{16}N_4O_7$ (340.3): C, 45.88; H, 4.73; N, 16.47. Found: C, 45.97; H, 4.84; N, 16.62.

*5-(2-Deoxy-*D*-lyxo-hex-1-enopyranosyl)tetrazole* (**24a**).—Yield: 79%; the compound did not melt till 360°C, but gradually decomposed; $[\alpha]_D$ +6° (*c* 1.5,

Me_2SO); ^1H NMR (Me_2SO-d_6): δ 12.2 (br s, 1 H, NH), 5.72 (br s, 1 H, H-2), 4.49 (br s, 1 H, H-3′), 4.23 (t, 1 H, H-5′), 3.73 (br s, 1 H, H-4′), 3.50, 3.45 (2 s, 2 H, H-6′a, 6′b), 5.2–3.0 (br s, 3 H, 3 OH); ^{13}C NMR (Me_2SO-d_6): δ 157.67 (C-5), 148.8 (C-1′), 100.73 (C-2′), 77.84, 64.05, 64.04 (C-3′,4′,5′), 60.57 (C-6′). Anal. Calcd for $C_7H_{10}N_4O_4$ (214.2): N, 26.16. Found: N, 25.90.

5-Methyl-2-(3,4,6-tri-O-acetyl-2-deoxy-D-lyxo-*hex-1-enopyranosyl)-1,3,4-oxadiazole* (**25**).—The unsaturated tetrazole **24** (3.4 g, 10 mmol) was heated with Ac_2O (8 mL, 90 mmol) on a water bath for 12 h. The solution was concentrated and codistilled with dry MeOH (3 × 10 mL). A solution of the residual syrup in $CHCl_3$ was washed with satd aq $NaHCO_3$ until neutral, dried, and evaporated. The residue was purified by column chromatography (1:1 benzene–ether) and the resulting syrup was crystallised from EtOH to give **25** (1.42 g, 40%), mp 150–151°C; $[\alpha]_D$ −71° (*c* 1.3, $CHCl_3$); ^1H NMR: δ 5.81 (dd,1 H, $J_{2',3'}$ 2.3, $J_{2',4'}$ 1.2 Hz, H-2′), 5.75 (ddd, 1 H, $J_{3',4'}$ 4, $J_{3',5'}$ 1 Hz, H-3′), 5.53 (ddd, 1 H, $J_{4',5'}$ 2 Hz, H-4′), 4.58 (dt, 1 H, $J_{5',6'b}$ 6.3 Hz, H-5′), 4.41 (dd, 1 H, $J_{5',6'a}$ 6.3 Hz, H-6′a), 4.31 (dd, 1 H, $J_{6'a,6'b}$ 12 Hz, H-6′b), 2.58 (s, 3 H, CH_3), 2.18, 2.14, 2.08 (3 s, 9 H, 3 Ac); ^{13}C NMR: δ 169.91 (C=O), 163.90 (C-5), 156.50 (C-2), 140.52 (C-1′), 103.27 (C-2′), 74.20, 64.10, 62.54 (C-3′,4′,5′), 61.21 (C-6′), 20.54 ($COCH_3$), 10.89 (CH_3). Anal. Calcd for $C_{15}H_{18}N_2O_8$ (354.3): C, 50.85; H, 5.12; N, 7.91. Found: C, 51.02; H, 5.17; N, 8.20.

2-(2-Deoxy-D-lyxo-*hex-1-enopyranosyl)-5-methyl-1,3,4-oxadiazole* (**25**a).—Yield: 79% (syrup); $[\alpha]_D$ −19° (*c* 1.3, Me_2SO); ^1H NMR (Me_2SO-d_6): δ 5.57 (br s, 1 H, H-2′), 4.8–4.3 (br s, 3 H, 3 OH), 4.40 (br dd, 1 H, H-3′), 4.03 (br t, 1 H, H-5′), 3.85 (br d, 1 H, H-4′), 3.72 (dd, 1 H, $J_{5',6'a}$ 6.4 Hz, H-6′a), 3.64 (dd, 1 H, $J_{5',6'b}$ 6.7, $J_{6'a,6'b}$ 11.1 Hz, H-6′b), 1.82 (s, 3 H, CH_3). Anal. Calcd for $C_9H_{12}N_2O_5$ (228.5): N, 12.27. Found: N, 12.01.

2-(3,4,6-Tri-O-acetyl-2-deoxy-D-lyxo-*hex-1-enopyranosyl)-5-trifluoromethyl-1,3,4-oxadiazole* (**26**).—To the unsaturated tetrazole **24** (3.4 g, 10 mmol) dissolved in $CHCl_3$ (5 mL) was added trifluoroacetic anhydride (3.53 mL, 25 mmol). The reaction started with vigorous gas evolution. After 1 h at room temperature, the solution was concentrated and coevaporated with dry MeOH (3 × 10 mL). Work-up as for **25** and crystallisation from EtOH yielded **26** (2.94 g, 72%); mp 112–114°C; $[\alpha]_D$ −66° (*c* 1.1, $CHCl_3$); ^1H NMR: δ 6.04 (dd, 1 H, $J_{2',3'}$ 2.7, $J_{2',4'}$ 1.5 Hz, H-2′), 5.79 (ddd, 1 H, $J_{3',4'}$ 4.5, $J_{3',5'}$ 1.3 Hz, H-3′), 5.57 (ddd, 1 H, $J_{4',5'}$ 1.5 Hz, H-4′), 4.63 (m, 1 H, H-5′), 4.42 (dd, 1 H, $J_{5',6'a}$ 6.5 Hz, H-6′a), 4.33 (dd, 1 H, $J_{5',6'b}$ 6.5, $J_{6'a,6'b}$ 11.9 Hz, H-6′b), 2.15, 2.12, 2.08 (3 s, 9 H, 3 Ac); ^{13}C NMR: δ 170.22, 169.81, 169.72 (C=O), 161.03 (C-2), 155.0 (q, $^2J_{C,F}$ 43 Hz, C-5), 139.67 (C-1′), 115.99 (q, $J_{C,F}$ 275 Hz, CF_3), 106.61 (C-2′), 74.68, 63.97, 62.34 (C-3′,4′,5′), 61.09 (C-6′), 20.46, 20.39 (CH_3). Anal. Calcd for $C_{15}H_{15}F_3N_2O_8$ (408.2): C, 44.13; H, 3.70; F, 13.96; N, 6.86. Found: C, 44.31; H, 3.73; F, 13.90, N, 6.75.

2-Chloromethyl-2-(3,4,6-tri-O-acetyl-2-deoxy-D-lyxo-*hex-1-enopyranosyl)-1,3,4-oxadiazole* (**27**).—A mixture of **24** (1.36 g, 4 mmol) and chloroacetyl chloride (3.2 mL, 40 mmol) was heated on a hot water bath for 1 h. The excess of the reagent was distilled off and toluene (2 × 5 mL) was evaporated from the syrupy residue.

Purification by silica gel chromatography with 6:2:2 benzene–ether–hexane and crystallisation from MeOH gave **27** (0.95 g, 61%); mp 128–129°C; $[\alpha]_D$ −47° (*c* 1.2, $CHCl_3$); ^1H NMR: δ 5.91 (dd, 1 H, $J_{2',3'}$ 2.4, $J_{2',4'}$ 1.2 Hz, H-2'), 5.77 (ddd, 1 H, $J_{3',4'}$ 3.7, $J_{3',5'}$ 1.2 Hz, H-3'), 5.55 (ddd, 1 H, $J_{4',5'}$ 1.2 Hz, H-4'), 4.73 (s, 2 H, CH_2Cl), 4.59 (m, 1 H, H-5'), 4.40 (dd, 1 H, $J_{5',6'a}$ 6.5 Hz, H-6'a), 4.32 (dd, 1 H, $J_{5',6'b}$ 6.6, $J_{6'a,6'b}$ 10.9 Hz, H-6'b), 2.13, 2.11, 2.07 (3 s, 9 H, 3 Ac); ^{13}C NMR: δ 170.40, 169.94 (C=O), 162.41 (C-5), 160.67 (C-2), 140.53 (C-1'), 104.79 (C-2'), 74.44, 64.11, 62.47 (C-3',4',5'), 61.20 (C-6', CH_2Cl), 20.59 (CH_3). Anal. Calcd for $C_{15}H_{17}ClN_2O_8$ (388.8): C, 46.33; H, 4.40; Cl, 9.12; N, 7.20. Found: C, 46.44; H. 4.37; Cl, 9.07; N, 7.15.

*5-Chloromethyl-2-(2-deoxy-*D-lyxo-*hex-1-enopyranosyl)-1,3,4-oxadiazole* (**27a**).–Yield: 60% (syrup); $[\alpha]_D$ −27° (*c* 1.2, Me_2SO); ^1H NMR (MeSO-d_6): δ 8.1–7.2 (br s, 3 H, 3 OH), 5.65 (br s, 1 H, H-2'), 5.31 (s, 2 H, CH_2Cl), 4.42 (br dd, 1 H, H-3'), 4.06 (br t, 1 H, H-5'), 3.87 (br d, 1 H, H-4'), 3.72 (dd, 1 H, $J_{5',6'a}$ 6.1 Hz, H-6'a), 3.65 (dd, 1 H, $J_{5',6'b}$ 6.4, $J_{6'a,6'b}$ 11.1 Hz, H-6'b). Anal. Calcd for $C_9H_{11}ClN_2O_5$ (262.6): Cl, 13.49; N, 10.66. Found: Cl, 13.17; N, 10.40.

*5-Ethoxycarbonyl-2-(3,4,6-tri-*O*-acetyl-2-deoxy-*D-lyxo-*hex-1-enopyranosyl)-1,3,4-oxadiazole* (**28**).—A mixture of **24** (0.34 g, 1 mmol) and ethyl oxalyl chloride (3.4 mL, 30 mmol) was heated on a hot water bath for 2 h. After cooling to room temperature, the solution was concentrated, and the residue was dissolved in $CHCl_3$. The solution was washed with satd aq $NaHCO_3$, dried, and concentrated. The residual syrup crystallised from EtOH to give **28** (0.264 g, 64%); mp 103–105°C $[\alpha]_D$ −60° (*c* 1.1, $CHCl_3$); ^1H NMR: δ 6.01 (dd, 1 H, $J_{2',3'}$ 3.8, $J_{2',4'}$ 1.6 Hz, H-2'), 5.73 (ddd, 1 H, $J_{3',4'}$ 4, $J_{3',5'}$ 1 Hz, H-3'), 5.50 (ddd, 1 H, $J_{4',5'}$ 1.6 Hz, H-4'), 4.62–4.23 (m, 5 H, H-5',6'a,6'b, $-CH_2-$), 2.09, 2.07, 2.03 (3 s, 9 H, 3 Ac), 1.43 (t, 3 H, *J* 7 Hz, CH_3); ^{13}C NMR: δ 170.23, 169.83, 169.74 (C=O), 160.83 ($O=\mathit{C}OC_2H_5$), 156.27 (C-5), 153.77 (C-2), 140.07 (C-1'), 106.13 (C-2'), 74.40, 63.98, 62.25 (C-3',4',5'), 63.61, 61.04 (C-6', $\mathit{C}H_2CH_3$), 20.52, 20.43, 20.38 ($CO\mathit{C}H_3$), 13.86 ($CH_2\mathit{C}H_3$). Anal. Calcd for $C_{17}H_{20}N_2O_{10}$ (412.3): C, 49.52; H, 4.88; N, 6.79. Found: C, 49.28; H, 4.79; N, 6.67.

*5-Carbamoyl-2-(2-deoxy-*D-lyxo-*hex-1-enopyranosyl)-1,3,4-oxadiazole* (**28a**).—Compound **28** (0.412 g, 1 mmol) was dissolved in abs MeOH saturated with NH_3 at 0°C, and the solution was kept at room temperature for 16 h. The deposited crystals were filtered off and recrystallised from MeOH to give **28a** (0.21 g, 82%); mp 115–116°C; [α[$_D$ −19° (*c* 1.8, Me_2SO); ^1H NMR (pyridine-d_5): δ 9.85, 9.60 (2 s, 2 H, NH_2), 6.31 (dd, 1 H, $J_{2',3'}$ ~ 2, $J_{2',4'}$ ~ 2 Hz, H-2'), 5.70–4.90 (br s, 3 H, 3 OH), 4.89 (dd, 1 H, $J_{4',5'}$ 2.5 Hz, H-4'), 4.62 (m, 1 H, H-5'), 4.59 (dd, 1 H, $J_{3',4'}$ 4 Hz, H-3'), 4.54 (dd, 1 H, $J_{5',6'a}$ 5.5 Hz, H-6'a), 4.51 (dd, 1 H, $J_{5',6'b}$ 6.5, $J_{6'a,6'b}$ 12 Hz, H-6'b). Anal. Calcd for $C_9H_{11}N_3O_6$ (257.2): N, 16.33. Found: N, 16.09.

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