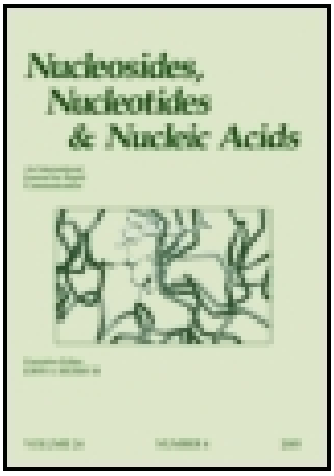

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PREPARATION AND UTILITY OF 5-β-D-RIBOFURANOSYL-1H-TETRAZOLE AS A KEY SYNTHON FOR C-NUCLEOSIDE SYNTHESIS

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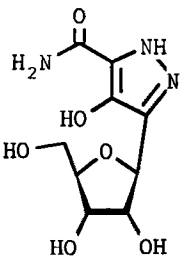
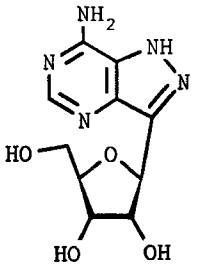
Abstract: A synthesis of 5-β-D-ribofuranosyl-1H-tetrazole (2) and 5-β-D-ribofuranosyl-1,3,4-oxadiazole-2(3H)-one (9) derivatives is described. Ring transformations of 2 have been investigated in an effort to establish the stability of this synthon for further use in dipolar cycloaddition reactions.

Introduction

Numerous synthetic routes have been explored leading to naturally occurring C-nucleosides[1a] and to their structurally related analogs.[1b,2] Of particular interest to us was the synthesis of formycin and pyrazofurin analogs which could be realized by elaboration of nitrogen heterocycle on a suitably modified carbohydrate moiety.



Pyrazofurin



Formycin

Various approaches have been reported for the synthesis of this kind of compound,[3,4,5] the most widely used being based on the β-oriented cyanoribosyl

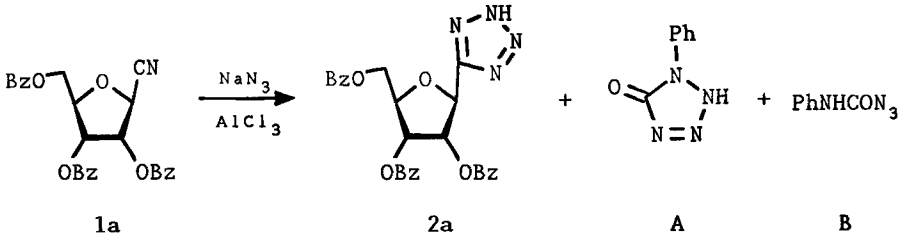
derivative **1a**, originally synthesized by Bobek and Farkaš.[6] Its preparation on the synthetic scale was improved by the reaction of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose with trimethylsilylcyanide in the presence of $SnCl_4$.[7] Several functionalized 3-ribosyl pyrazoles have been prepared from **1a** *via* the reaction of sugar diazoalkanes with substituted acetylenes or olefins.[9] The multistage nature of this synthesis suggested an alternative route *via* nitrilimines generated *in situ* from 5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1H-tetrazole (**2a**). Indeed, attempts at a thermal degradation of N-2 silylated derivative of **2a** in the presence of diethyl fumarate or diethyl acetylenedicarboxylate afforded the corresponding Δ^2-pyrazolines and pyrazole derivatives, but unfortunately with poor yields.[11] The poor yields obtained in these initial investigations discouraged the further use of **2a** at that time. However, our success in using **2a** in reactions with substituted 2-chloropyridines[12] prompted us to initiate investigations designed to optimize the 1,3-dipolar cycloaddition chemistry of ribofuranosyl nitrilimines, since all of the known cycloaddition routes met the demands for stereochemical control at the anomeric center.[13,14]

We now wish to report an alternative synthesis of **2** with special emphasis on some configurational assignments. Several blocking groups were introduced, the selection being predicated primarily on their use in future ribose moiety transformations, or to prevent elimination of *O*-acyl groups usually removed when drastic conditions were used. Additionally, chemical transformations of tetrazole **2** were investigated in order to prove or disprove the feasibility of stereocontrolled reaction sequences when reacting **2** as a ribofuranose dipole D-allononitrilimine.

Various aglycone transformations of 2-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-furan[15] and 6-hydroxy-6-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)pyran-3(2H,6H)-one[16] as examples of similar approaches to the C-nucleoside synthesis was undertaken by Maeba *et al.*[17]

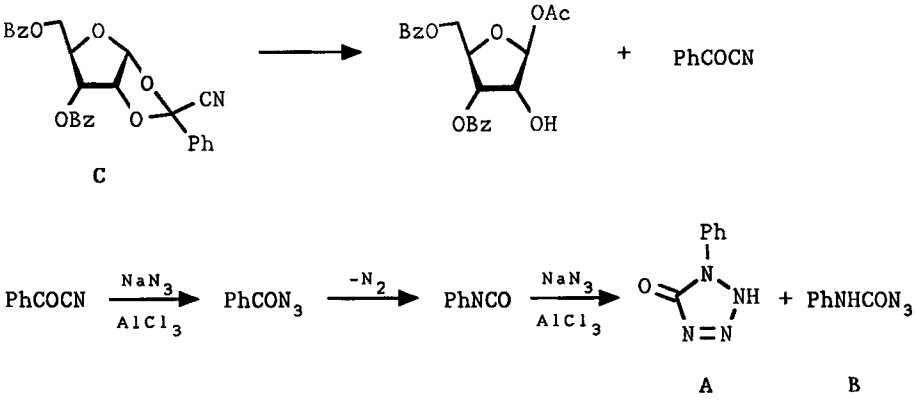
5-β-D-Ribofuranosyl-1H-tetrazole (2c)

Tetrazoles are readily available in excellent yields from suitably protected 2,5-anhydro-D-allononitriles.[10,11] For example 2,5-anhydro-3,4,6-tri-*O*-benzoyl-D-allononitrile (**1a**) was reacted with either NH_4Cl/NaN_3 in DMF or $AlCl_3/NaN_3$ in THF to afford **2a**. The first reaction furnished a 100% yield of **2a** (and provides strong support for its potential use as a nitrilimine precursor in a well-defined configuration), whereas 1-phenyl-5(4H)-tetrazolinone (**A**) and phenylcarbamoyl-



1a 2a A B

Figure 1



A B

Figure 2

azide (**B**), isolated as byproducts, considerably lowered the yield of **2a** obtained by the second procedure (Figure 1). This pathway can be explained by the separation of a CN^- ion, which can act as a nucleophile on an acyloxonium ion to form **C**, an 1,2-*O*-cyanobenzylidene derivative (Figure 2). This derivative was finally transformed to **A** and **B** through a number of consecutive reactions.

It is worth noting that an analogous reaction using 2,5-anhydro-3,4,6-tri-*O*-benzoyl-D-gluconitrile afforded a noticeable quantity of **A** merely as a by-product,[18] whereas in the proposed scheme, phenylcarbamoylazide was apparently formed directly from aluminium azide and phenylisocyanate, generated *in situ* from **C**. This reaction was not observed by Horwitz *et al*,[19] but was observed when trimethylsilylazide was used.[20] Recently the intermediate **C** was isolated when trimethylsilylcyanide and 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose were reacted at room temperature in the presence of $SnCl_2$. The intermediate **C** was

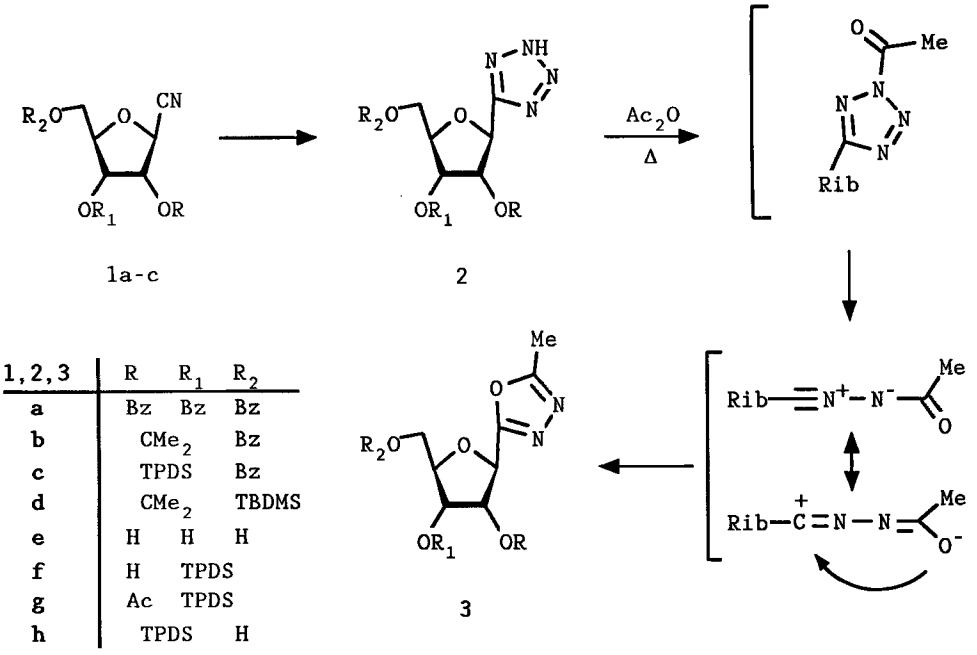
further transformed to **1a** at 70 °C in the presence of excess trimethylsilylcyanide.[7a,b]

Our attempts to obtain **C** by simulating the above reaction conditions (starting with 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose, NaCN, $AlCl_3$ and NaN_3) failed, and instead of **C**, 2,3,5-tri-*O*-benzoyl-β-D-ribofuranosylazide[21] was obtained in 50% yield. The yield of the azide was improved (80%) when we used an equivalent amount of trimethylsilylcyanide. It is of interest that the azide was obtained only in a 6% yield in the absence of cyanide from the reaction mixture. **C** seemed quite stable under the reaction conditions (THF, $AlCl_3$, reflux).

At relatively moderate temperature (> 100 °C), elimination of benzoic acid was observed in reactions of **2a** with activated halogen heterocycles[12b] and 1,3-dipolar cycloadditions with alkynes and olefins.[11] Therefore, before we continued these studies, a complete evaluation of general protection and deprotection reactions was undertaken. At the same time, with the introduction of these new blocking groups, additional supporting data on the configuration of starting materials and final products, as well as nitrilimines, could be provided by the application of the Imbach rule or several other criteria.[22,23,24]

Isopropylidenation of deprotected **2c** was unsuccessful, and an alternative route was considered. When **1b**[8] was treated with NaN_3/NH_4Cl in DMF, **2b** was obtained in good yield (67%) ($\Delta\delta(CMe_2)$ being 0.19). The $\Delta\delta$ value for the compound does not allow unequivocal assignment of anomeric configuration on the basis of the Imbach rule. Yet subsequent debenzoylation of **2b** in methanolic NaOMe and further treatment of the resulting product with *tert*-butyldimethylsilylchloride yielded well-defined derivative **2d** with $\Delta\delta(CMe_2)$ value 0.24, which is indicative of the β-configuration. When debenzoylation of **2b** was followed by treatment with Dowex H^+, **2c** was obtained. Furthermore, **2c** was stirred with equimolar amounts of 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane ($TPDSCl_2$)[25] in dry pyridine for 2 hours to afford **2f** as a foam (in 90% yield). On the other hand, **1c** was prepared from 2,5-anhydro-6-*O*-benzoyl-D-allononitrile,[8] which was transformed ($TMSN_3$, $SnCl_4$, toluene, r.t.) to **2c**. Debenzoylation of **2c** afforded **2h**, different from **2f**. The structures were proved by conversion of **2f** to **2h**, which was achieved with pyridinium chloride in DMF[26] (Figure 3).

This possible migration could be avoided by protecting the 2'-position in **2f**. Acetylation with acetic anhydride seemed a reasonable reaction when possible degradation of a tetrazole ring by the formation of 1,3,4-oxadiazole (Huisgen reaction)[27] was prevented. Indeed, **3g** was obtained when **2f** was heated at reflux in



1,2,3	R	R_1	R_2
a	Bz	Bz	Bz
b	CMe_2		Bz
c	TPDS		Bz
d	CMe_2		TBDMS
e	H	H	H
f	H	TPDS	
g	Ac	TPDS	
h	TPDS		H

Figure 3

Ac_2O for 30 minutes, while **2g** was isolated when **2f** was stirred with Ac_2O in pyridine at room temperature. In fact, these 3',5'-*O*-TPDS derivatives (**2f**, **2g** and **3g**) with respective coupling constants $J_{1',2'}$ < 1.0 (Me_2SO-d_6), < 1.5 (Me_2CO-d_6) and 1.5 Hz ($CDCl_3$), allowed another convenient β-configuration assignment.[23] **2d** was transformed to **3d** (boiling Ac_2O), and it could be readily concluded that no anomerization had taken place, since the $\Delta\delta(CMe_2)$ was still within the limits for the β-configuration[22,24] (0.19 ppm). The deprotection of TBDMS and the isopropylidene group of **3d** with Bu_4NF in THF and by subsequent treatment with aq. HCl afforded **3c** in a β-configuration. An identical product was obtained by deprotection of 2-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (**3a**) or 2-(5-*O*-benzoyl-2,3-*O*-TPDS-β-D-ribofuranosyl)-1,3,4-oxadiazole (**3c**) with NaOMe.

In addition to experiments with Ac_2O, reactions with chloro- and cyanoformate esters were also studied. We reported on the alkylation properties of chloro- and cyanoformate esters at an earlier date.[28] It is well known that even activated carbonitriles and carbonyl groups are less reactive dipolarophiles than olefins and alkynes. The main products of alkylations of silylated tetrazole **2a** with

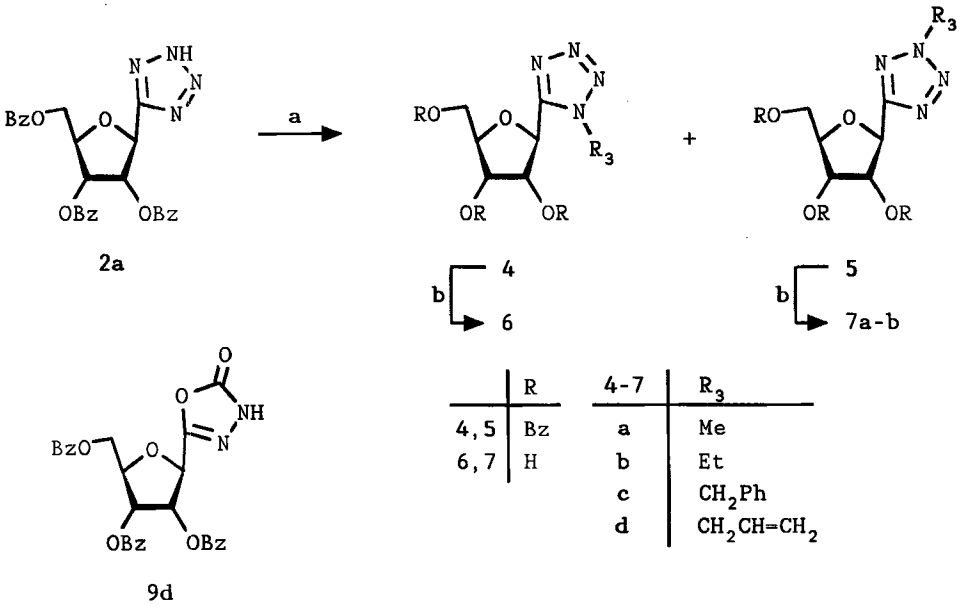
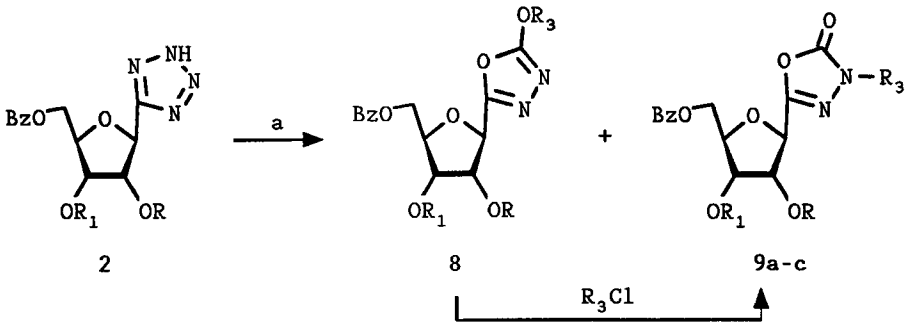


Figure 4

primary alkyl (methyl, ethyl, benzyl, and allyl) chloro- and/or cyanoformates were N-1 and N-2 alkyl substituted 5-glycosyl tetrazoles **4** and **5**, which were further transformed with methanolic NaOMe into 1- and 2-alkyl-5-(β-D-ribofuranosyl)-tetrazoles **6** and **7** (Figure 4). On the other hand, catalytic transformation ($BF_3.Et_2O$) of **2a** with benzyl chloroformate afforded cycloadduct **9d** (20%) in addition to the major products 1- and 2-benzyl tetrazoles **4c** and **5c**, whereas Lewis acids like $SnCl_4$ and $SbCl_5$ did not succeed in turning the reaction pathway into rearrangement.

The structures of **4** and **5** were proved by alkylations of tetrazole **2a** with alkylation agents such as diazomethane and N,N-dimethylformamide diethyl acetal and determined from ^1H and ^{13}C NMR data. In proton NMR spectra, anomeric proton downfield shifts of 0.1 ppm were observed for N-2 substituted tetrazoles **5** in comparison to N-1 isomers **4**. H-2', H-3' chemical shift differences ($\Delta\delta_{H\text{-}2'H\text{-}3'}$) for **5** and **4** are < 0.07 and 0.33 ± 0.06 ppm, respectively. ^{13}C NMR peaks belonging to C-5, C-1' and C-1" are also significant for the site of substitution assignment. C-5



2	R	R_1
a	Bz	Bz
b	CMe_2	
c	TPDS	

8,9	R	R_1	R_3
a	Bz	Bz	CH_2CCl_3
b	Bz	Bz	CMe_2CCl_3
c	Bz	Bz	Menthyl
d	Bz	Bz	Ph
e	CMe_2		Ph
f	TPDS		Ph
g	Bz	Bz	CHMeEt
h	TPDS		$CH=CH_2$
i	Bz	Bz	$CH=CH_2$

a. i HMDS,Δ;
ii $ClCOOR_3$,Py,toluene,Δ;

Figure 5

for **4** and **5** resonate at 151.46 ± 0.22 and 163.63 ± 0.17 ppm respectively, whereas anomeric carbons resonate at 73.65 ± 0.11 and 75.30 ± 0.08 ppm respectively. Alkyl C-1 is shifted by 5.30 ± 0.24 ppm to the lower field with N-2 substitution in comparison to N-1. Two aromatic peaks in ^{13}C NMR spectrum of **9d** at 153.39 and 154.37 ppm, as well as two sharp bands in carbonyl region at 1820 and 1789 cm^{-1}, besides benzoyl CO at 1728 cm^{-1} in the IR spectrum, confirm the presence of oxadiazolone aglycone in the molecule.

In contrast to the above-mentioned formates (esters of primary alcohols), no alkylations were observed when 5-glycosyltetrazoles **2** reacted with secondary (2-butyl, (-)-menthyl), tertiary (2-trichloromethyl-2-propyl) or electronegatively substituted primary alkyl (2,2,2-trichloroethyl), alkenyl (vinyl) or aryl (phenyl) chloroformates.[28] O-2 substituted 1,3,4-oxadiazoles **8** were isolated. The mechanism of transformation **2** → **8** is likely to be similar to the rearrangement **2** → **3**. In cases of **8a-c**, consecutive thermal rearrangements[29] of alkyl substituents, due to alkyl chlorides generated from chloroformates, afforded N-3 substituted isomers **9a-c**

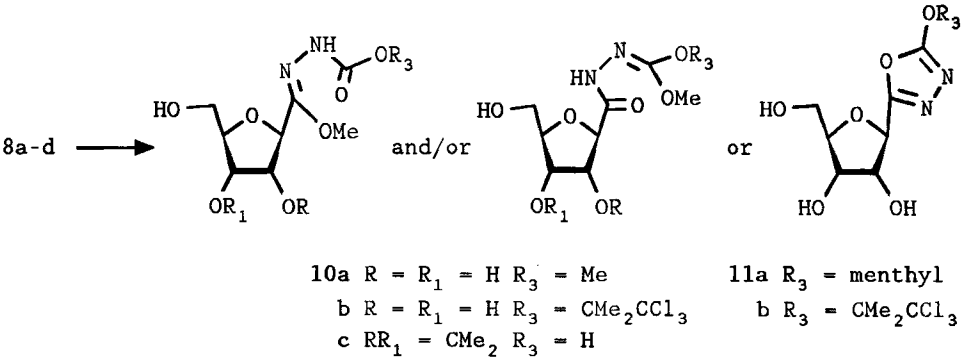


Figure 6

(Figure 5). Transformations were completed in boiling toluene and pyridine in 4 hours or less, with 50-90% yields. The influence of the sugar protection on the reaction time and yield was observed in the case of phenyl chloroformate as a dipolarophile; the reaction with 2',3',5'-tri-*O*-benzoyl glycoside **2a** was terminated in 4 hours in 50% yield, with 2',3'-*O*-isopropylidene-5'-*O*-benzoyl **2b** in 1 hour in 60% yield, and with 2',3'-*O*-TPDS-5'-*O*-benzoyl **2c** in 0.5 hour in 70% yield. Structures of **8** and **9** were determined by ^{1}H and ^{13}C NMR and IR spectroscopy. Anomeric carbons of **8** (with tri-*O*-benzoyl protected sugar moiety) and **9** resonate at 83.06 ± 0.56 and at 74.39 ± 0.19 ppm respectively. A substituted nitrogen atom causes downfield shifts of C-1 and H-1 of the substituent in comparison to oxygen atom (*e.g.* 80.63 and 5.03 ppm respectively of 2,2,2-trichloroethyl for **8a** in comparison to 75.88 and 4.84 ppm respectively for **9a**). In ^{13}C NMR spectra, due to adjacent "pyrrole" nitrogen, C-2 of N-3 substituted oxadiazole derivatives **9a-c** appear at higher field (with δ 147.32, 145.94 and 151.86) than the corresponding C-2 of O-substituted isomers **8a-c** (with δ 159.27, 158.68 and 157.82).

2-Alkoxyoxadiazoles **8** were subjected to base catalyzed deprotection of the sugar moiety (Figure 6). Debenzoylation with methanolic NaOMe, as well as the attempts at molecular sieves (4Å, powder) in MeOH were usually accompanied by ring opening of the aglycone, thus yielding substituted 2,5-anhydro-D-allonohydrazides **10**. 2-Trichloromethyl-2-propoxy derivative **10b** was isolated as a mixture of two thermally stable isomers (in a 6/4 ratio). But with 2-menthyloxy derivative **8c**, no ring opening was observed, and 2-menthyloxy-5-(β-D-ribofuranosyl)-1,3,4-oxadiazole (**11a**) was isolated. 2-[2-(Trichloromethyl-2-propoxy)]-5-

(β-D-ribofuranosyl)-1,3,4-oxadiazole (**11b**) was obtained from **8b** by deprotection with methanolic ammonia.

It is evident that the use of nitrilimines generated from 5-(β-D-ribofuranosyl)-1H-tetrazole is a synthetically useful process for the design of novel C-nucleosides, and will be furthermore adopted for the synthesis of carbocyclic C-nucleosides.[30] Additional findings in exploring the transformations leading to pyrazolo[4,3-c]-pyridine C-nucleosides will be presented elsewhere.

Experimental Part

Abbreviations. -DMFDEA, N,N-dimethylformamide diethyl acetal; HMDS, hexamethyldisilazane; TBDMS, *tert*-butyldimethylsilyl; $TMSN_3$, trimethylsilyl-azide; TPDS, 1,1,3,3-tetraisopropyldisiloxane-1,3-diyl-; $TPDSCl_2$, 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane.

Materials and methods - Toluene and pyridine were dried by refluxing over KOH and BaO respectively, and then distilled; DMF was dried over BaO and distilled under reduced pressure. NaN_3 and NH_4Cl were dried in *vacuo* at 100 °C over P_2O_5. Ion exchanger Dowex H^+ (50WX8, Fluka) was washed with MeOH prior to use. Other solvents and reagents were of commercial purity. Evaporations were conducted with a rotary evaporator under reduced pressure. Flash chromatography was carried out on Silica gel 60 (40-63 μm, Merck) and analytical TLC on precoated plates Silica gel 60 F_{254} (Merck). The spots were visualized by irradiation with UV light (254 nm) or by spraying with 3.5% phosphomolybdic acid in ethanol and heating or by exposing to iodine vapours.

Melting points were determined on a Kofler apparatus and are uncorrected. IR spectra were obtained using Bio-Rad FTS 15/80 spectrophotometer. Mass spectra were recorded on a VG Autospec Q spectrometer at the Jožef Stefan Institute, Ljubljana. Microanalyses were performed at the Department of Chemistry, University of Ljubljana and at the Institute of Organic Chemistry, Karl-Franz University, Graz. Optical rotations were measured on a Perkin Elmer 241 MC polarimeter. NMR spectra were recorded using a Varian VXR-300 instrument (^1H at 299.94 and ^{13}C at 75.43 MHz) if not stated or a Jeol FX 90Q (^{13}C at 22.50 MHz) or a Varian EM 360-L (^1H at 60 MHz) spectrometer. Me_4Si and solvents were used as internal references for ^1H and ^{13}C ($CDCl_3$, 77.00 ppm; Me_2SO-d_6, 39.50 ppm; Me_2CO-d_6, δ_{CD_3} 29.80) measurements respectively. Chemical shifts and coupling constants were obtained from a first order analysis of the spectra. The

spectra were assigned by means of the corresponding ^{1}H-^{1}H and ^{13}C-^{1}H chemical shift correlated spectra.

2,5-Anhydro-6-*O*-benzoyl-3,4-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-D--allononitrile (1c). -A mixture of 2,5-anhydro-6-*O*-benzoyl-D-allononitrile[8] (3.17 g, 12 mmol) in pyridine (30 ml) and $TPDSCl_2$ (3.9 ml, 12.4 mmol) was stirred at r.t. for one day. Pyridinium chloride was filtered off, the filtrate once coevaporated with toluene and the residue partitioned between EtOAc (100 ml) and water (15 ml). The organic layer was washed with 5% aq. HCl (3x15 ml), sat. aq. $NaHCO_3$ (3x15 ml), and brine (10 ml), dried (Na_2SO_4) and concentrated to give glassy **1c** (5.85 g, 96%). An analytical sample was purified by chromatography on silica gel with $CHCl_3$/n-hexane (1:2) to give, after slow evaporation of solvent, crystalline product **1c** (large transparent plates) with m.p. 49-51 °C. ^{1}H-NMR ($CDCl_3$) δ 1.05 (m, 28H, 4 i-Pr), 4.31(m, 1H, H-5), 4.47(dd, 1H, H-6a), 4.50(dd, 1H, H-4), 4.55(dd, 1H, H-6b), 4.61(d, 1H, H-2), 4.69(t, 1H, H-3), 7.45, 7.58, and 8.05(3m, 5H, Ph); $J_{2,3}$ 4.3, $J_{3,4}$ 4.5, $J_{4,5}$ 5.9, $J_{5,6a}$ 4.1, $J_{5,6b}$ 3.5, $J_{6a,6b}$ 12.3 Hz. ^{13}C-NMR ($CDCl_3$) δ 12.62, 12.65, 13.00, and 13.16(4 $\underline{C}HMe_2$), 16.77, 16.83, 16.91, 16.97, 17.05, 17.10, and 17.26(4 $CH\underline{Me}_2$), 63.39(C-6), 71.12(C-2), 73.97(C-4), 77.09(C-3), 82.78(C-5), 117.10(C-1), 128.37, 129.36, 129.62, and 133.22(Ph), 166.14(CO). HRMS (FAB): m/z MH^+ calcd for $C_{25}H_{40}NO_6Si_2$ 506.239, found 506.239. *Anal.* Calcd for $C_{25}H_{39}NO_6Si_2$ (505.77): C, 59.37; H, 7.77; N, 2.77. Found: C, 59.32; H, 7.84; N, 2.88.

5-(2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosyl)-1H-tetrazole (2a). *Method A.* -To a solution of allononitrile **1a**[7c] (23.57 g, 0.05 mol) in DMF (125 ml) NaN_3 (3.90 g, 0.06 mol) and NH_4Cl (3.29 g, 0.06 mol) were added. The reaction mixture was stirred at 110-120 °C for 5 h, then filtered and concentrated. The residue was partitioned between EtOAc (600 ml) and water (100 ml). Aqueous layer was extracted with EtOAc (100 ml). Organic layers were gathered and washed with 5% aq. HCl (3x100 ml), sat. aq. $NaHCO_3$ (100 ml) and brine (100 ml), dried (Na_2SO_4) and concentrated to give **2a** as a pale yellow foam (51.40 g, 100%). ^{1}H-NMR (DMSO-d_6) δ 4.58(dd, 1H, H-5'), 4.61(dd, 1H, H-5"), 4.81(m, 1H, H-4'), 5.69(d, 1H, H-1'), 5.95(t, 1H, H-2'), 6.05(t, 1H, H-3'), 7.46, 7.65, and 7.90(3m, 15H, 3 Ph); $J_{1',2'}$ 4.7 Hz. ^{13}C-NMR (DMSO-d_6) δ 64.62(C-5'), 72.84(C-3'), 75.35(C-2'), 75.52(C-1'), 78.68(C-4'), 128.56, 128.27, 128.82, 129.33, 129.39, 133.48, and 133.82(3 Ph), 158.42(C-5), 164.86, 164.91, and 165.65(3 CO). *Anal.* Calcd for $C_{27}H_{22}N_4O_7$ (514.50): C, 63.03; H, 4.31; N, 10.89. Found: C, 62.78; H, 4.58; N, 10.56. An analytical sample was purified by chromatography on silica gel with CH_2Cl_2 and CH_2Cl_2/MeOH (20:1 and 10:1).

Method B -To a solution of **1a** (5.6 g, 11.9 mmol) in dry THF (30 ml) anhydrous $AlCl_3$ (1.57 g, 11.8 mmol) and NaN_3 (3.38 g, 50 mmol) were added. The resulting suspension was heated at reflux for 20 h. The cooled reaction mixture was then acidified with 15% aq. HCl (18 ml) and the organic layer separated. It was extracted with EtOAc (3x60 ml) and the combined organic fractions dried ($MgSO_4$). The solvent was evaporated and the residue triturated with $CHCl_3$. The white crystals, which had separated, were collected to yield 300 mg of 1-phenyl-5(4H)-tetrazolinone (**A**), m.p. 187-190 °C (lit.[18] 189-190 °C), MS m/z 162(M^+). The filtrate was concentrated to dryness on a steam bath and the glassy residue triturated with hot water until **A** was separated (200 mg). The total yield of **A** was 500 mg (26%). The residue obtained by the above purification procedure was dissolved in CH_2Cl_2 and dried ($MgSO_4$). The evaporated residue was chromatographed on a Sephadex LH 20 column (3x50 cm) with CH_2Cl_2 to give phenylcarbamoylazide (**B**) (200 mg, 10%), m.p. 105-106 °C (ligroin) (lit.[31] 107 °C), IR (KBr) ν 2145(N_3), 1695(CO); and with $CHCl_3$ (50 ml) and $CHCl_3$/MeOAc (30:1) (50 ml) to give **2a** (3.24 g, 53%) as a white foam.

5-(5-*O*-Benzoyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)-1H-tetrazole (2b). -To a solution of allononitrile **1b**[8] (6.11 g, 20.2 mmol) in DMF (50 ml) NaN_3 (1.7 g, 26 mmol) and NH_4Cl (1.4 g, 26 mmol) were added. The reaction mixture was stirred at 100 °C for 3 h, then filtered and concentrated. The evaporated residue was partitioned between EtOAc (200 ml) and water (15 ml). The organic layer was washed with water (5x15 ml), dried (Na_2SO_4) and concentrated to give **2b** as a white foam (4.7 g, 67%). ^{1}H-NMR ($CDCl_3$) δ 1.36 and 1.55(2s, 6H, CMe_2), 4.27(dd, 1H, H-5'), 4.34(dd, 1H, H-5"), 4.60(m, 1H, H-4'), 4.98(dd, 1H, H-3'), 5.26(dd, 1H, H-2'), 5.41(d, 1H, H-1'), 7.47, 7.65, and 7.72(3m, 5H, Ph); $J_{1',2'}$, 3.2, $J_{2',3'}$, 6.2, $J_{3',4'}$, 2.4, $J_{4',5'}$, and $J_{4',5"}$ 4.2, $J_{5',5"}$ 12.0 Hz. ^{13}C-NMR ($CDCl_3$) δ 25.28 and 27.16($C\underline{Me}_2$), 64.98(C-5'), 78.67(C-1'), 81.68(C-3'), 84.77(C-4'), 85.02(C-2'), 114.86($\underline{C}Me_2$), 128.56, 128.76, 129.63, and 133.76(Ph), 156.20(C-5), 167.26(CO). HRMS: m/z M^+-Me calcd for $C_{15}H_{15}N_4O_5$: 331.1042, found 331.1039. *Anal.* Calcd for $C_{16}H_{18}N_4O_5 \times \frac{1}{3} CH_2Cl_2$: C, 52.36; H, 5.02; N, 14.95. Found: C, 52.38; H, 5.21; N, 14.78. An analytical sample was purified by chromatography on silica gel with CH_2Cl_2, CH_2Cl_2/MeOH (20:1 and 10:1).

5-[5-*O*-Benzoyl-2,3-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl]-1H-tetrazole (2c). -To a solution of allononitrile **1c** (3.58 g, 7.9 mmol) in toluene (40 ml) $TMSN_3$ (5.3 ml, 40 mmol) and anhydrous $SnCl_4$ (0.75 ml, 6.4 mmol) were added and the mixture stirred at r.t. for 5 h. Another portion of

$TMSN_3$ (2.6 ml, 20 mmol) and anhydrous $SnCl_4$ (0.4 ml, 3.4 mmol) was added and stirring continued for 14 h. The catalyst was neutralized with sat. aq. $NaHCO_3$ (180 ml) and after the addition of 10 g of celite the mixture vigorously stirred and filtered through a celite pad. The pad was washed with EtOAc (100 ml). Organic layer was separated from water, washed with brine (50 ml), dried (Na_2SO_4) and concentrated to give 2c (3.96 g, 91%) as a white foam. ^{1}H-NMR ($CDCl_3$) δ 0.92(m, 28H, 4 i-Pr), 4.17(m, 2H, H-4', H-3'), 4.45(m, 2H, H-5', H-5"), 4.77(t, 1H, H-2'), 5.17(d, 1H, H-1'), 7.06, 7.22, and 7.60(3m, 5H, Ph); $J_{1',2'}$, 2.2 Hz. ^{13}C-NMR ($CDCl_3$) δ 12.67, 12.82, 13.35, and 13.41(4 $\underline{C}HMe_2$), 17.00, 17.13, and 17.40(4 $CH\underline{Me}_2$), 64.45(C-5'), 74.10(C-3'), 76.70(C-2'), 80.13(C-1'), 81.57(C-4'), 127.31, 128.14, 128.38, 129.05, 129.59, and 133.15(Ph), 160.01(C-5), 167.64(CO). MS: m/z 505(M^+- *i*-Pr). *Anal.* Calcd for $C_{25}H_{40}N_4O_6Si_2$ (548.79): C, 54.72; H, 7.35; N, 10.21. Found: C, 54.53; H, 7.37; N, 9.99.

5-(5-*O*-*t*-Butyldimethylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)-1H-tetrazole (2d). -To a solution of **2b** (4.2 g, 12 mmol) in methanol (30 ml) 1.3 M methanolic NaOMe (10 ml) was added and stirred at r.t. overnight. Then the reaction mixture was neutralized with Dowex H^+, filtered and concentrated. The residue was chromatographed on silica gel (100 g) with $CHCl_3$ (1 l) and $CHCl_3$/ MeOH (5:1) (1.5 l) to give 2.5 g (10.3 mmol) of 5-(2,3-*O*-isopropylidene-β-D-ribofuranosyl)-1H-tetrazole, which was stirred in pyridine (40 ml) with TBDMSCl (1.7 g, 11.3 mmol) at r.t. for 8 h. Pyridinium chloride was filtered off, the solution concentrated and coevaporated with toluene (to remove pyridine). The evaporated residue was partitioned between EtOAc (200 ml) and water (30 ml). The organic layer was washed with water (2x15 ml), dried (Na_2SO_4) and concentrated to give **2d** (3.2 g, 74%) as a white foam. ^{1}H-NMR ($CDCl_3$) δ 0.18 and 0.20(2s, 6H, $SiMe_2$), 0.95(s, 9H, CMe_3), 1.36 and 1.60(2 s, 6H, CMe_2), 3.77(dd, 1H, H-5'), 4.03(dd, 1H, H-5"), 4.39(m, 1H, H-4'), 4.76(dd, 1H, H-3'), 4.85(dd, 1H, H-2'), 5.63(d, 1H, H-1'), 12.7(br s, 1H, NH); $J_{1',2'}$, 1.5, $J_{2',3'}$, 5.7, $J_{3',4'}$, 3.3, $J_{4',5'}$, 3.3, $J_{4',5"}$ 2.6, $J_{5',5"}$ 11.8 Hz. ^{13}C-NMR ($CDCl_3$) δ -5.45($SiMe_2$), 18.49($\underline{C}Me_3$), 25.38 and 27.31($C\underline{Me}_2$), 25.93 ($C\underline{Me}_3$), 64.15(C-5'), 78.26(C-1'), 80.81(C-3'), 85.73(C-2'), 86.7(C-4'), 114.09 ($\underline{C}Me_2$), 156.85(C-5). HRMS: m/z (M^+-Me) calcd for $C_{14}H_{25}N_4O_4Si$ 341.1645, found 341.1653. *Anal.* Calcd for $C_{15}H_{28}N_4O_4Si \times 0.3\ CH_2Cl_2$: C, 48.11; H, 7.55; N, 14.67. Found: C, 48.23; H, 7.74; N, 14.41. An analytical sample was purified by chromatography on silica gel with CH_2Cl_2 and CH_2Cl_2/ MeOH (20:1 and 10:1).

5-(β-D-Ribofuranosyl)-1H-tetrazole (2e). *Method A*: -To a mixture of **2a** (10.28 g, 20 mmol) in MeOH (100 ml) 1.2 M methanolic NaOMe (50 ml) was

added and heated at reflux for 5 min. The cooled solution was acidified with Dowex H^+, stirred at r.t. for 2 h, filtered and concentrated. The oily residue was coevaporated few times with water (to remove MeOBz). Lyophilization afforded **2c** (3.5 g, 87%) as a colorless hygroscopic foam. $[\alpha]_D^{23}$ -31.3° (c 0.96, Me_2SO). ^{1}H-NMR (DMSO-d_6) δ 3.47(dd, 1H, H-5'), 3.58(dd, 1H, H-5"), 3.91(m, 2H, H-3', H-4'), 4.18(t, 1H, H-2'), 4.98(d, 1H, H-1'); $J_{1',2'}$, 5.9 Hz. ^{13}C-NMR (DMSO-d_6) δ 61.63(C-5'), 70.22(C-3'), 76.10(C-2'), 78.87(C-1'), 83.32(C-4'), 161.88(C-5). MS: m/z 202(M^+). *Anal.* Calcd for $C_6H_{10}N_4O_4$ (202.17): C, 35.65; H, 4.99; N, 27.71. Found: C, 35.77; H, 5.05; N, 27.73. An analytical sample was purified by chromatography on silica gel with CH_2Cl_2 and CH_2Cl_2/MeOH (20:1 and 5:1).

Method B: -A methanolic solution of 5-(2,3-*O*-isopropylidene-β-D-ribofuranosyl)-1H-tetrazole obtained from **2b** (*vide supra)* was acidified with Dowex H^+ and stirred at r.t. for 2 h. The mixture was filterd and few times coevaporated with water (to remove MeOBz) to give **2c** identical to the product obtained by Method A.

5-[3,5-*O*-(1,1,3,3-Tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl]-1H-tetrazole (2f). -A mixture of **2c** (1.41 g, 7 mmol) in pyridine (15 ml) and $TPDSCl_2$ (2.23 ml, 7 mmol) was stirred at r.t. for 1.5 h, then filtered and concentrated. The foamy residue was partitioned between water (15 ml) and EtOAc (80 ml). The organic layer was washed with 5% aq. HCl (2x10 ml) and sat. aq. $NaHCO_3$ (2x10 ml), dried (Na_2SO_4) and concentrated to give **2f** (2.8 g, 90%) as a hygroscopic colorless foam. ^{1}H-NMR (DMSO-d_6) δ 0.98(m, 28H, 4 i-Pr), 3.86(m, 3H, H-5', H-5", H-4'), 4.29(d, 1H, H-2'), 4.55(dd, 1H, H-3'), 4.94(s, 1H, H-1'); 5.3(br s, 2H, NH, OH); $J_{1',2'}$, <1.0, $J_{2',3'}$, 4.9, $J_{3',4'}$, 4.6 Hz. ^{13}C-NMR (DMSO-d_6) δ 12.08, 12.18, 12.61, and 12.81(4 $\underline{C}HMe_2$), 19.91, 19.94, 17.02, 17.15, 17.19, 17.22, 17.25, and 17.35(4 $CH\underline{Me}_2$), 62.79(C-5'), 73.47(C-3'), 74.92(C-2'), 78.14(C-1'), 80.48(C-4'), 159.15(C-5). MS: m/z 401(M^+-Pr^i). *Anal.* Calcd for $C_{18}H_{36}N_4O_5Si_2$ (444.68): C, 48.62; H, 8.16; N, 12.60. Found: C, 48.61; H, 8.28; N, 12.62. An analytical sample was purified by chromatography on silica gel with $CHCl_3$ and $CHCl_3$/MeOH (20:1).

5-[2-*O*-Acetyl-3,5-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl]-1H-tetrazole (2g). -A mixture of **2f** (0.5 g, 1.1 mmol) in pyridine (3 ml) and Ac_2O (0.4 ml) was stirred at r.t. for 1 h, then concentrated and few times coevaporated with MeOH. The residue was dissolved in EtOAc (30 ml) and washed with sat. aq. $NaHCO_3$ (5 ml) and brine (5 ml), dried (Na_2SO_4) and concentrated. The residue was chromatographed on silica gel (20 g) with CH_2Cl_2 (0.3 l) and CH_2Cl_2/MeOH (5:1) (0.4 l) to give, after concentation, **2g** (0.4 g, 73%) as a colorless foam.

Anal. Calcd for $C_{20}H_{38}N_4O_6Si_2$ (486.72): C, 49.36; H, 7.87; N, 11.51. Found: C, 49.25; H, 8.04; N, 11.42.

5-[2,3-*O*-(1,1,3,3-Tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl]-1H-tetrazole (2h). *Method A*: -A mixture of **2f** (0.5 g, 1.1 mmol) in DMF (5 ml) and pyridinium chloride (0.25 g, 2.2 mmol) was stirred at r.t. overnight, then filtered and concentrated. The oily residue was partitioned between EtOAc (30 ml) and water (10 ml). The organic layer was washed with water (10 ml) and brine (10 ml) and dried (Na_2SO_4). Concentration afforded the title compound **2h** (0.42 g, 84%) as a colorless glass. *Anal.* Calcd for $C_{18}H_{36}N_4O_5Si_2$ (444.68): C, 48.62; H, 8.16; N, 12.60. Found: C, 48.37; H, 8.41; N, 12.88.

Method B: -To a solution of tetrazole **2c** (0.5 g, 0.9 mmol) in MeOH (10 ml) methanolic solution of NaOMe (20 mg Na/5 ml MeOH) was added and stirred at r.t. for 1 h. Then the reaction mixture was neutralized with Dowex H^+, filtered and concentrated. The residue was chromatographed on silica gel (50 g) with CH_2Cl_2 (100 ml) and CH_2Cl_2/MeOH (5:1) (100 ml) to give **2h** 0.35 g (88%) as a colorless glass.

2-Methyl-5-glycosyl-1,3,4-oxadiazoles (3a,c,d,g). *General Method:* -A mixture of 5-glycosyl-1H-tetrazole (**2**), Ac_2O (2 ml per mmol), and hydroquinone (1 mg per mmol) was heated at reflux for the stated period (0.5-1.5 h), concentrated and co-evaporated few times with MeOH. The residue was dissolved in $CHCl_3$ (20 ml per mmol), washed with sat. aq. $NaHCO_3$ (2x5 ml per mmol) and brine (5 ml per mmol), dried (Na_2SO_4), concentrated and chromatographed on silica gel with CH_2Cl_2 to give the title compounds **3a,c,d,g**.

2-Methyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (3a). -Reaction time with **2a**: 1 h. The oily product obtained after chromatography was coevaporated few times with MeOH until white solid **3a** separated (3.1 g, 60%), m.p. 138-139 °C (MeOH) (ref.[32] 139-140°C). ^{1}H-NMR ($CDCl_3$) δ 2.37(s, 3H, Me), 4.58(dd, 1H, H-5'), 4.77(m, 1H, H-4'), 4.88(dd, 1H, H-5"), 5.52(d, 1H, H-1'), 5.98(t, 1H, H-3'), 6.07(t, 1H, H-2'), 7.39, 7.47, 7.58, 7.96, and 8.12(5m, 15H, 3 Ph); $J_{1',2'}$ 6.0, $J_{4',5'}$ 3.5, $J_{4',5"}$ 3.2, $J_{5',5"}$ 12.0 Hz. ^{13}C-NMR ($CDCl_3$) δ 10.74(Me), 63.46(C-5'), 72.54(C-3'), 73.89(C-2'), 74.11(C-1'), 81.13(C-4'), 128.41, 128.46, 128.67, 129.41, 129.69, 129.74, 133.26, and 133.63(3 Ph), 162.86, 164.99, 165.21, and 165.95(3 CO, C-2, C-5).

5-[5-*O*-Benzoyl-2,3-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl)-2-methyl-1,3,4-oxadiazole (3c). -Reaction time with **2c**: 1.5 h. Yield 73%,

pale yellow stiff syrup. *Anal.* Calcd for $C_{27}H_{42}N_2O_7Si_2$ (562.82): C, 57.62; H, 7.52; N, 4.98. Found: C, 57.54; H, 7.41; N, 5.09.

5-(5-*O*-*t*-Butyldimethylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)-2-methyl-1,3,4-oxadiazole (3d). -Reaction time with **2d**: 1.5 h. Yield 65%, white foam. MS: m/z 370(M^+). *Anal.* Calcd for $C_{17}H_{30}N_2O_5Si$ (370.52): C, 55.10; H, 8.16; N, 7.56. Found: C, 55.01; H, 7.92; N, 7.85.

2-Methyl-5-(β-D-ribofuranosyl)-1,3,4-oxadiazole (3c). *Method A*: -A mixture of oxadiazole **3a** (1.58g, 3 mmol) in methanolic NaOMe (150 mg Na/45 ml MeOH) was stirred at r.t. for 0.5 h, then acidified with Dowex H^+, filtered, concentrated and coevaporated with water (to remove MeOBz). Stirring of the residue with EtOEt afforded **3c** (0.44 g, 67%) as a white solid, m.p. 115-117 °C (ref.[31] 110 °C). ^{1}H-NMR (DMSO-d_6) δ 2.51(s, 3H, Me), 3.42(m, 1H, H-5'), 3.51(m, 1H, H-5"), 3.87(m, 1H, H-4'), 3.97(m, 1H, H-3'), 4.27(m, 1H, H-2'), 4.77(d, 1H, H-1'), 4.81(t, 1H, OH-5'), 5.16(d, 1H, OH-3'), 5.40(d, 1H, OH-2'); $J_{1',2'}$, 6.2 Hz. ^{13}C-NMR (DMSO-d_6) δ 10.63(Me), 61.75(C-5'), 71.26(C-3'), 73.94(C-2'), 74.88(C-1'), 85.87(C-4'), 164.62, 164.83(C-2, C-5). MS: m/z 216(M^+). *Anal.* Calcd for $C_8H_{12}N_2O_5$ (216.19): C, 44.45; H, 5.59; N, 12.96. Found: C, 44.28; H, 5.47; N, 12.95.

Method B: -A mixture of oxadiazole **3c** (65 mg, 0.10 mmol) in MeOH and methanolic NaOMe (2 mg Na/0.5 ml MeOH) was stirred at r.t. for 2 d, then acidified with Dowex H^+, filtered and concentrated. The residue was chromatographed on silica gel (10 g) with CH_2Cl_2 (100 ml) and of CH_2Cl_2/MeOH (5:1) (50 ml) to give **3c** (12 mg, 56%).

Method C: -A mixture of oxadiazole **3d** (415 mg, 1.1 mmol) in 1M Bu_4NF/THF (2 ml) was stirred at r.t. overnight. The evaporated residue was dissolved in $CHCl_3$ (10 ml) and washed with aq. HCl (pH 4, 3x3 ml), sat aq. $NaHCO_3$ (3 ml), and brine (3 ml), dried (Na_2SO_4) and concentrated to give, after chromatographic treatment of crude product (*vide supra*), **3c** (200 mg, 83%).

5-[2-*O*-Acetyl-3,5-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl]-2-methyl-1,3,4-oxadiazole (3g). -Reaction time with **2f**: 0.5 h. Yield 70%, colorless stiff syrup which slowly solidified. MS: m/z 457(M^+-Pr^i). *Anal.* Calcd for $C_{22}H_{40}N_2O_7Si_2$ (500.75): C, 52.77; H, 8.05; N, 5.59. Found: C, 52.71; H, 8.03; N, 5.79.

N-Trimethysilyl-5-glycosyltetrazole. *General Procedure.* -A mixture of 5-glycosyl-1H-tetrazole **2** and HMDS (5 ml per 1 mmol) was heated at reflux for 2 d. The excessive HMDS was distilled off under anhydrous conditions.

1- and 2-Methyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)tetrazole (4a and 5a). *Method A.* -A mixture of 5 mmol of silylated tetrazole (from 2.57 g of **2a**) in pyridine (10 ml) and methyl chloroformate (0.95 g, 10 mmol) was stirred at r.t. for 5 d. Additional portion of ester (0.95 g) was added and stirring continued for 5 d. Reaction mixture was concentrated and the residue partitioned between EtOAc (150 ml) and water (30 ml). The organic layer was washed with 5% aq. HCl (3x20 ml), sat. aq. $NaHCO_3$ (2x20 ml), and brine (20 ml), dried (Na_2SO_4) and concentrated. The residue was chromatographed on silica gel (300 g) with $CHCl_3$ /EtOAc (50:1) (3 l) to give, after treatment with MeOH, **5a** (1.14 g, 43%) and **4a** (0.40 g, 15%) as white solids, m.p. 83-85 °C and 133-134 °C respectively.

(**4a**) ^{1}H-NMR ($CDCl_3$) δ 4.12(s, 3H, Me), 4.57(dd, 1H, H-5'), 4.78-7.83(m, 2H, H-4', H-5"), 5.60(d, 1H, H-1'), 5.99(t, 1H, H-3'), 6.23(t, 1H, H-2'), 7.41, 7.45, 7.58, and 7.98(4m, 15H, 3 Ph); $J_{1',2'}$, 4.7, $J_{2',3'}$, and $J_{3',4'}$, 5.4, $J_{4',5'}$, 4.0, $J_{5',5"}$ 12.3 Hz. ^{13}C-NMR ($CDCl_3$) δ 34.31(Me), 63.21(C-5'), 71.91(C-3'), 73.55(C-1'), 74.34(C-2'), 81.17 (C-4'), 128.45, 128.48, 128.54, 128.61, 128.97, 129.51, 129.70, 129.74, 133.40, 133.62, and 133.70(3 Ph), 151.71(C-5), 165.14 and 165.16(3 CO). *Anal.* Calcd for $C_{28}H_{24}N_4O_7$ (528.52): C, 63.63; H, 4.58; N, 10.60. Found: C, 63.81; H, 4.52; N, 10.47.

(**5a**) ^{1}H-NMR ($CDCl_3$) δ 4.27(s, 3H, Me), 4.61(dd, 1H, H-5'), 4.79(m, 1H, H-4'), 4.81(dd, 1H, H-5"), 5.65(d, 1H, H-1'), 6.03(t, 1H, H-3'), 6.08(t, 1H, H-2'), 7.39, 7.56, 7.96, and 8.10(4m, 15H, 3 Ph); $J_{1',2'}$, 5.7 Hz. ^{13}C-NMR ($CDCl_3$) δ 39.37(Me), 63.69(C-5'), 72.40(C-3'), 75.01(C-2'), 75.22(C-1'), 80.19(C-4'), 128.21, 128.29, 128.31, 128.72, 129.52, 129.58, 129.61, 132.98, 133.38, and 133.41(3 Ph), 163.66(C-5), 165.00, 165.14, and 166.00(3 CO). *Anal.* Calcd for $C_{28}H_{24}N_4O_7$ (528.52): C, 63.63; H, 4.58; N, 10.60. Found: C, 63.84; H, 4.67; N, 10.75.

Method B. -A solution of 10 ml of 0.24 N CH_2N_2 in 1,2-dimethoxyethane was added to the solution of **2a** (1.01 g, 2 mmol) in 1,2-dimethoxyethane (5 ml) and stirred at r.t. overnight. Chromatography of the evaporated residue (*vide supra*) afforded **5a** (0.72 g, 68%) and **4a** (0.09 g, 8%).

1- and 2-Ethyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)tetrazole (4b and 5b). *Method A.* -A mixture of 2.5 mmol of silylated tetrazole (from 1.30 g of **2a**) and 5 ml of ethyl cyanoformate was stirred at 75 °C for 18 h. Evaporated residue was chromatographed subsequently on two silica gel columns (200 g) with $CHCl_3$ to give **5b** (0.75 g, 55%) and **4b** (0.16 g, 11%) as white solids, m.p. 99-101 °C and 124.5-125.5 °C respectively. MS: m/z (**4b**) 542(M^+); (**5b**) 542(M^+). *Anal.* Calcd for $C_{29}H_{26}N_4O_7$ (542.55): C, 64.20; H, 4.83; N, 10.33. Found: (**4b**) C, 64.05; H, 4.96; N, 10.49; (**5b**) C, 64.30; H, 4.84; N, 10.35.

Method B. A mixture of 2a (0.51 g, 1 mmol) in DMF (5 ml) and DMFDEA (0.54 g, 3 mmol) was stirred overnight at r.t. Chromatographic separation (*vide supra*) of the evaporated residue afforded **5b** (0.29 g, 53%) and **4b** (0.03 g, 6%).

1- and 2-Benzyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)tetrazole (4c and 5c). Benzyl chloroformate (1.6 ml, 11 mmol) was added dropwise into a boiling mixture of 9.7 mmol of silylated tetrazole (from 4.99 g of **2a**) in toluene (20 ml) and pyridine (1.0 ml, 11 mmol) and heated at reflux for 18 h. The reaction mixture was filtered, concentrated and partitioned between EtOAc (100 ml) and water (20 ml). The organic layer was washed with 5% aq. HCl (2x15 ml), sat. aq. $NaHCO_3$ (2x15 ml), and brine (15 ml), dried (Na_2SO_4) and concentrated. Chromatography on silica gel (500 g) with benzene/EtOAc (50:1), (11 l) afforded **5c** (3.22 g, 56%) and **4c** (1.25 g, 21%) as stiff syrups. 4c was obtained as a white solid by treatment with MeOH, m.p. 108-111 °C. *Anal.* Calcd for $C_{34}H_{28}N_4O_7$ (604.63): C, 67.54; H, 4.67; N, 9.27. Found: (4c) C, 67.49; H, 4.68; N, 9.45; (5c) C, 67.80; H, 4.66; N, 9.49.

Method B. A mixture of 2 mmol of silylated tetrazole (from 1.03 g of **2a**) in toluene (15 ml) and benzyl cyanoformate (0.44 ml, 3 mmol) was heated at reflux for 3 h, then concentrated and chromatographed on silica gel (*vide supra*) to give **5c** (0.53 g, 44%) and **4c** (0.44 g, 36%).

$BF_3.Et_2O$ Catalyzed Reaction of Benzyl Chloroformate with 5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1H-tetrazole (2a). 5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole-2(3H)-one (9d). A mixture of **2a** (1.03 g, 2 mmol) in toluene (10 ml), benzyl chloroformate (0.68 g, 4 mmol), and $BF_3.Et_2O$ (0.30 g, 2 mmol) was heated at reflux for 4 h. The catalyst and the ester were added in two equal portions (0.86 g and 0.30 g, respectively) in 5 h's interval and heating continued overnight. The reaction mixture was treated then in the same way as in the case of noncatalyzed reaction of benzyl chloroformate with **2a** (*vide supra*). Chromatography provided **5c** (0.54 g, 45%), **4c** (0.06 g, 5%) and **9d** (0.21 g, 20%; foam). (**9d**) ^1H NMR (60 MHz, $CDCl_3$) δ 4.56(m, 3H, H-4', H-5', H-5"), 5.11(d, 1H, H-1'), 5.87(dd, 1H, H-3'), 5.97(dd, 1H, H-2'), 7.40 and 7.95(2m, 15H, 3 Ph); $J_{1'2'}$, 4.5 Hz. ^{13}C NMR (22.50 MHz, $CDCl_3$) 63.46(C-5'), 72.34, 73.10, 75.16(C-3', C-2', C-1'), 80.58(C-4'), 126.36, 128.36, 129.23, 129.66, 133.13, and 133.56(3 Ph), 153.39 and 154.37(C-2, C-5), 164.98 and 166.17(3 COPh). IR (KBr) ν 1813, 1782, 1728, 1451, 1311, 1273, 1180, 1119, 1096, 1072, 1026, 710. HRMS (FAB): m/z MH^+ calcd for $C_{28}H_{23}N_2O_9$ 531.140, found 531.141. *Anal.* Calcd for $C_{28}H_{22}N_2O_9$ (530.50): N, 5.28. Found: N, 5.50.

1- and 2-Allyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)tetrazole (4d and 5d). A mixture of 8 mmol of silylated tetrazole (from 4.12 g of **2a**) in toluene (30 ml), pyridine (0.73 ml, 9 mmol), and allyl chloroformate (0.96 ml, 9 mmol) was heated at reflux for 1d. Another portion of ester (0.53 ml, 5 mmol) and pyridine (0.40 ml, 5 mmol) was added and heating continued for 4 h. The evaporated residue was partitioned between EtOAc (150 ml) and water (50 ml). The organic layer was washed with 5% aq. HCl (20 ml), sat. aq. $NaHCO_3$ (20 ml), and brine (20 ml), dried (Na_2SO_4) and concentrated. Chromatography on silica gel (250 g) with benzene/EtOAc (50:1), (4 l) afforded **5d** (1.70 g, 38%) and **4d** (0.43 g, 10%) as white solids, m.p. 93-96 °C (MeOH) and 79-83 °C (EtOH) respectively. MS: m/z (**4d**) 554(M^+), (**5d**) 554(M^+). *Anal.* Calcd for $C_{30}H_{26}N_4O_7$ (554.56): C, 64.98; H, 4.73; N, 10.10. Found: (4d) C, 64.99; H, 4.85; N, 10.24; (5d) C, 64.87; H, 4.67; N, 10.04.

1- and 2-Alkyl-5-(β-D-ribofuranosyl)tetrazoles (6 and 7) from 1- and 2-Alkyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)tetrazoles (4 and 5). *General method.* 1 mmol of **4** or **5** in 0.2 M methanolic NaOMe (15 ml) was stirred at r.t. for 1 h. The reaction mixture was neutralized with Dowex H^+, filtered, and concentrated. The evaporated residue was coevaporated few times with water (to remove MeOBz) to give **6** or **7** as a colorless stiff syrup in 80-90% yield.

1-Methyl-5-(β-D-ribofuranosyl)tetrazole (6a). ^{1}H NMR (DMSO-d_6) δ 3.40-3.57(m, 2H, H-5', H-5"), 3.89(m, 1H, H-4'), 4.00(m, 1H, H-3'), 4.09(s, 3H, Me), 4.40(m, 1H, H-2'), 4.78(t, 1H, OH-5'), 5.03(d, 1H, H-1'), 5.13(d, 1H, OH-3'), 5.37(d, 1H, OH-2'); $J_{1',2'}$, 5.8, $J_{2'OH-2'}$, 6.1, $J_{3'OH-3'}$, 5.4, $J_{5'OH-5'}$, and $J_{5"OH-5'}$, 5.5 Hz. ^{13}C NMR (DMSO-d_6) δ 35.04(Me), 62.02(C-5'), 71.66(C-3'), 74.70 and 74.91(C-1', C-2'), 86.40(C-4'), 154.77(C-5). HRMS (FAB): m/z MH^+ calcd for $C_7H_{13}N_4O_4$ 217.0937, found 217.0944.

2-Methyl-5-(β-D-ribofuranosyl)tetrazole (7a). ^{1}H NMR (DMSO-d_6, D_2O) δ 3.43(dd, 1H, H-5'), 3.50(dd, 1H, H-5"), 3.85(m, 1H, H-4'), 3.99(t, 1H, H-3'), 4.26(t, 1H, H-2'), 4.36(s, 3H, Me), 4.85(d, 1H, H-1'); $J_{1',2'}$, 6.3 Hz. ^{13}C NMR (DMSO-d_6) δ 39.50(Me), 62.13(C-5'), 71.36(C-3'), 74.67(C-2'), 75.43(C-1'), 85.56(C-4'), 165.04(C-5). *Anal.* Calcd for $C_7H_{12}N_4O_4$ (216.20): C, 38.89; H, 5.59; N, 25.91. Found: C, 38.62; H, 5.47; N, 26.26.

1-Ethyl-5-(β-D-ribofuranosyl)tetrazole (6b). MS: m/z 230(M^+). *Anal.* Calcd for $C_8H_{14}N_4O_4$ (230.23): C, 41.73; H, 6.12; N, 24.33. Found: C, 41.74; H, 6.11; N, 23.93.

2-Ethyl-5-(β-D-ribofuranosyl)tetrazole (7b). MS: m/z 230(M^+), 127(B+30). *Anal.* Calcd for $C_8H_{14}N_4O_4$ (230.23): C, 41.73; H, 6.12; N, 24.33; Found: C, 41.52; H, 5.93; N, 24.26.

2-Benzyl-5-(β-D-ribofuranosyl)tetrazole (7c). HRMS: m/z M^+ calcd for $C_{13}H_{16}N_4O_4$ 292.1171, found 292.1175. *Anal.* Calcd for $C_{13}H_{16}N_4O_4$ (292.30): C, 53.42; H, 5.52; N, 19.17. Found: C, 53.33; H, 5.66; N, 19.10.

2-Allyl-5-(β-D-ribofuranosyl)tetrazole (7d). HRMS: m/z M^+ calcd for $C_9H_{14}N_4O_4$ 242.101, found 242.101. *Anal.* Calcd for $C_9H_{14}N_4O_4$ (242.24): C, 44.63; H, 5.83. Found: C, 44.70; H, 5.88.

Substituted 5-Glycosyl-2-oxo-1,3,4-oxadiazoles (8 and 9) by Cycloaddition of N-Trimethylsilyl-5-glycosyltetrazoles with Chloroformate Esters. *General Procedure.* -Chloroformate ester (1.1-2.0 eq.) was added dropwise into a boiling mixture of N-trimethylsilyl-5-glycosyltetrazole (obtained from **2** with HMDS, *vide supra*) in toluene (5 ml per mmol) and pyridine (1.1-2.0 eq.) and heated at reflux for an indicated period of time. The evaporated residue was partitioned between EtOAc and water and the organic layer washed with (5% aq. HCl), sat. aq. $NaHCO_3$, and brine, dried (Na_2SO_4), concentrated and chromatographed on silica gel.

2-(2,2,2-Trichloroethoxy)-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (8a) and 3-(2,2,2-Trichloroethyl)-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole-2(3H)-one (9a). -Reaction time with silylated tetrazole (from **2a**) and 2,2,2-trichloroethyl chloroformate: 1h. Yield after chromatography with benzene/EtOAc (50:1) **9a**, 10%; white foam and **8a**, 47%; solid, m.p. 118-120°C (MeOH). IR (KBr) ν (**8a**) 2925, 1717, 1617, 1574, 1396, 1372, 1349, 1321, 1287, 1210, 1154, 1123, 1060, 908, 869, 798, 718; (film) ν (**9a**) 2927, 1773, 1729, 1616, 1576, 1450, 1363, 1314, 1268, 1182, 1119, 1098, 1071, 1026, 824, 711. *Anal.* Calcd for $C_{30}H_{23}N_2O_9Cl_3$ (661.84): C, 54.44; H, 3.50; 4.23. Found: (**8a**) C, 54.60; H, 3.48; N, 4.43; (**9a**) C, 54.77; H, 3.24; N, 4.21.

2-(2-Trichloromethyl-2-propoxy)-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (8b) and 3-(2-Trichloromethyl-2-propyl)-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole-2(3H)-one (9b). -Reaction time with silylated tetrazole (from **2a**) and 2-trichloromethyl-2-propyl chloroformate: 0.5 h. Yield after chromatography with benzene/EtOAc (50:1) **9b**, 13%; white solid, m.p. 114-118 °C (MeOH) and **8b**, 76%; white solid 130-131 °C (MeOH). IR (KBr) ν (**8b**) 1727, 1607, 1572, 1452, 1310, 1149, 1072, 803, 712; (**9b**) 1802, 1772, 1732, 1265, 1130, 1102, 798, 710. MS (FAB): m/z (**8b**) 691(MH^+); (EI): m/z (**9b**) 690(M^+). *Anal.* Calcd for

$C_{32}H_{27}N_2O_9Cl_3$ (689.94): C, 55.71; H, 3.94; N, 4.06. Found: (**8b**) 55.35; H, 4.03; N, 4.26; (**9b**) C, 55.64; H, 3.96; N, 4.10.

2-Menthyloxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (8c) and 3-Menthyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole-2(3H)-one (9c). -Reaction time with silylated tetrazole (from **2a**) and (-)-menthyl chloroformate: 2.5 h. Yield after chromatography with benzene/EtOAc (50:1) **9c**, 4%; white foam and **8c**, 47%; white solid, m.p. 113-114 °C (MeOH).

(**8c**) ^{1}H-NMR ($CDCl_3$) δ 0.79 and 0.91(2d, 6H, CH<u>Me</u>$_2$), 0.94(m, 1H, H-4a"), 0.93(d, 3H, CH<u>Me</u>), 1.12(m, 2H, H-6a", H-3a"), 1.54(m, 2H, H-5", H-2"), 1.72(m, 2H, H-4b", H-3b"), 2.02(m, 1H, C<u>H</u>Me$_2$), 2.35(m, 1H, H-6b"), 4.63(dd, 1H, H-5a'), 4.75(m, 1H, H-4'), 4.79(m, 2H, H-5b', H-1"), 5.43(d, 1H, H-1'), 5.95(t, 1H, H-3'), 6.04(t, 1H, H-2'), 7.37, 7.47, 7.55, 7.95, and 8.13(5m, 15H, 3 Ph); $J_{1',2'}$, 5.7 Hz. ^{13}C-NMR ($CDCl_3$) δ 16.15 and 20.56(CH<u>Me</u>$_2$), 21.77(CH<u>Me</u>), 23.06(C-3"), 25.78 (<u>C</u>HMe$_2$), 31.22(C-5"), 33.79(C-4"), 39.56(C-6"), 47.24(C-2"), 63.63(C-5'), 72.35(C-3'), 73.56(C-2'), 74.49(C-1'), 80.76(C-4'), 84.90(C-1"), 128.36, 128.48, 128.63, 129.35, 129.63, 129.71, 133.08, 133.53, and 133.56(3 Ph), 157.82 and 166.06(C-2, C-5), 164.89, 165.10, and 166.10(3 <u>CO</u>Ph). IR (KBr) ν 2955, 1728, 1613, 1573, 1452, 1316, 1271, 1120, 1071, 943, 711. MS (FAB): m/z 669 (MH^+). *Anal.* Calcd for $C_{38}H_{40}N_2O_9$ (668.75): C, 68.25; H, 6.03; N, 4.19. Found: C, 68.04; H, 5.99; N, 4.48.

(**9c**) ^{1}H-NMR ($CDCl_3$) δ 0.77 and 0.87(2dd, 6H, CH<u>Me</u>$_2$), 0.86(m, 1H, H-4a"), 1.01(m, 2H, H-3a", H-6a"), 1.27(m, 1H, H-2"), 1.37(m, 1H, H-5"), 1.63(m, 2H, H-4b", H-3b"), 1.88(m, 1H, C<u>H</u>Me$_2$), 2.03(m, 1H, H-6b"), 4.59(dd, 1H, H-5a'), 4.68(m, 1H, H-4'), 4.72(m, 1H, H-1"), 4.82(dd, 1H, H-5b'), 5.23(d, 1H, H-1'), 5.93(m, 2H, H-2', H-3'), 7.31-7.54, 7.95, and 8.13(3m, 15H, 3 Ph); $J_{1',2'}$, 5.5 Hz. ^{13}C-NMR ($CDCl_3$) δ 16.12 and 20.46(CH<u>Me</u>$_2$), 21.67(CH<u>Me</u>), 23.16(C-3"), 25.98 (<u>C</u>HMe$_2$), 31.09(C-5"), 33.82(C-4"), 40.68(C-6"), 46.86(C-2"), 63.61(C-5'), 72.41(C-3'), 72.70(C-2'), 76.53(C-1"), 80.69(C-4'), 82.50(C-1'), 128.20, 128.25, 128.57, 128.65, 133.00, 133.34, and 133.50(3 Ph), 151.86, 164.78, 164.85, 165.00, and 165.81 (C-2, C-5, 3<u>CO</u>Ph). IR (KBr) ν 2955, 2927, 2870, 1830, 1733, 1723, 1604, 1495, 1452, 1374, 1314, 1268, 1179, 1121, 1098, 1028, 711. HRMS (FAB): m/z MH^+ calcd for $C_{38}H_{41}N_2O_9$ 669.281, found 669.283. *Anal.* Calcd for $C_{38}H_{40}N_2O_9$ × 0.3 $CHCl_3$: C, 65.29; H, 5.77; N, 3.98. Found: C, 65.14; H, 6.07; N, 3.95. An analytical sample was purified by chromatography on silica gel with n-hexane/$CHCl_3$ (3:2).

2-Phenyloxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (8d). -Reaction time with silylated tetrazole (from **2a**) and phenyl chloroformate: 4h. Yield after chromatography with CH_2Cl_2 93%, stiff syrup, which crystallized in few

days, m.p. 129.5-131.5 °C (MeOH). MS: m/z 606(M^+). *Anal.* Calcd for $C_{34}H_{26}N_2O_9$ (606.59): C, 67.32; H, 4.32; N, 4.62. Found: C, 67.17; H, 4.15; N, 4.65.

2-Phenyloxy-5-(5-*O*-benzoyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)-1,3,4-oxadiazole (8c). -Reaction time with silylated tetrazole (from **2b**) and phenyl chloroformate: 1 h. Yield after chromatography with CH_2Cl_2 60%, stiff syrup. MS: m/z 438(M^+). *Anal.* Calcd for $C_{23}H_{22}N_2O_7$ (438.44): C, 63.01; H, 5.06; N, 6.39. Found: C, 63.50; H, 4.91; N, 6.12.

2-Phenyloxy-5-[5-*O*-benzoyl-2,3-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl)-1,3,4-oxadiazole (8f). -Reaction time with silylated tetrazole (from **2d**) and phenyl chloroformate: 0.5 h. Yield after chromatography with CH_2Cl_2 70%, stiff syrup. HRMS (FAB): m/z MH^+ calcd for $C_{32}H_{45}N_2O_8Si_2$ 641.271, found 641.271. *Anal.* Calcd for $C_{32}H_{44}N_2O_8Si_2$ (640.89): N, 4.37. Found: N, 4.30.

2-(2-Butoxy)-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (8g). -Reaction time with silylated tetrazole (from **2a**) and 2-butyl chloroformate: 3.5 h. Yield after chromatography with CH_2Cl_2 and coevaporation of the resulting foam with MeOH 70%, white solid, m.p. 66-86 °C. *Anal.* Calcd for $C_{32}H_{30}N_2O_9$ (586.60): C, 65.52; H, 5.15; N, 4.78. Found: C, 65.71; H, 5.25; N, 4.98.

2-Vinyloxy-5-[5-*O*-benzoyl-2,3-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl)-1,3,4-oxadiazole (8h). -Reaction time with silylated tetrazole (from **2d**) and vinyl chloroformate: 1.5 h. Yield after chromatography with benzene/EtOAc (50:1) 62%, stiff syrup. HRMS: m/z M^+-Pr^i calcd for $C_{25}H_{35}N_2O_8Si_2$ 547.193, found 547.193. *Anal.* Calcd for $C_{28}H_{42}N_2O_8Si_2$ (590.83): N, 4.74. Found: N, 4.87.

2-Vinyloxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (8i). -Reaction time with silylated tetrazole (from **2a**) and vinyl chloroformate: 2 h. Yield after chromatography with CH_2Cl_2 54%, foam; MS: m/z 556(M^+). *Anal.* Calcd for $C_{30}H_{24}N_2O_9$ (556.53): C, 64.75; H, 4.35; N, 5.03. Found: C, 65.26; H, 3.99; N, 5.17.

Transformations of 2-Alkoxy/Aryloxy-5-glycosyl-1,3,4-oxadiazoles (8). A -With NaOMe. *General Procedure.* -A mixture of **8** (1.5 mmol) in 40 ml of 0.1 M methanolic NaOMe was stirred at r.t. for a given period of time, then acidified with Dowex H^+, and concentrated. The product **10** or **11** was isolated by (chromatography and) precipitation with the appropriate solvent. **B -With Molecular Sieves.** *General Procedure.* -A mixture of **8** (0.4 mmol) in MeOH (10 ml) and molecular sieves (powder, 4Å) was stirred at r. t. for 2 d, filtered through a celite pad, and evaporated. Further purification afforded **10**.

N'-Dimethoxymethylidene-2,5-anhydro-D-allonohydrazide (10a). -The evaporated residue obtained by procedure B (from 0.26 g of **8a**) was treated with MeOH to give **10a** (60 mg, 57%) as a white solid, m.p. 172-174 °C. ^{1}H-NMR (Me_2SO-d_6) δ 3.51(1H, H-6a), 3.68(dd, 1H, H-6b), 3.76 and 3.77(2s, 6H, 2 OMe), 3.38(m, 1H, H-5), 3.89(dd, 1H, H-4), 3.96(dd, 1H, H-3), 4.14(d, 1H, H-2), 5.05(br s, 3H, 3 OH), 9.76(br s, 1H, NH); $J_{2,3}$ 1.6, $J_{3,4}$ 4.6, $J_{4,5}$ 8.8, $J_{5,6a}$ 2.2, $J_{5,6b}$ 2.9, $J_{6a,6b}$ 11.7 Hz. ^{13}C-NMR (Me_2SO-d_6) δ 55.51 and 56.16(2 OMe), 59.26(C-6), 69.57(C-4), 74.79(C-3), 82.35(C-2), 83.85(C-5), 153.20 and 165.26(C-1, C=N). HRMS: m/z MH^+ calcd for $C_9H_{17}N_2O_7$ 265.1036, found 265.1040.

N'-[Methoxy-(2-trichloromethyl-2-propoxy)methylidene]-2,5-anhydro-D-allonohydrazide (10b-I and -II). -Using procedure A, **8b** (1.04 g) was transformed in 2.5 h into a pair of isomers **10b-I** and **-II** (in a 6/4 ratio) which was isolated without a separation, by chromatography on silica gel (20 g) with CH_2Cl_2 (0.2 l) and CH_2Cl_2/MeOH (5:1) (0.2 l), precipitation with EtOEt (ice bath), and filtration under the N_2 atmosphere, as a white solid (0.27 g, 44%), m.p. 152-158 °C (acetone). ^{1}H-NMR (Me_2SO-d_6, D_2O) δ (**10b-I**) 1.74 and 1.77(2s, 6H, CMe_2), 3.42-3.71(m, 2H, H-6a, H-6b), 3.76(m, 1H, H-5), 3.80(s, 3H, OMe), 3.97(m, 2H, H-3, H-4), 4.06(d, 1H, H-2); $J_{2,3}$ 3.1 Hz; (**10b-II**) 1.90(s, 6H, CMe_2), 3.42-3.71(m, 2H, H-6a, H-6b), 3.76(m, 1H, H-5), 3.77(s, 3H, OMe), 3.89(dd, 1H, H-4), 3.97(m, 1H, H-3), 4.15(d, 1H, H-2); $J_{2,3}$ 1.6 Hz. ^{13}C-NMR (Me_2SO-d_6, D_2O) δ (**10b-I**) 20.37 and 20.50(CMe_2), 56.32(OMe), 60.78(C-6), 70.40(C-4), 75.04(C-2), 83.51(C-5), 91.64 (CCl_3), 106.17(O<u>C</u>Me_2), 149.84(C-1), 166.64(CO); (**10b-II**) 22.27 and 22.90(C<u>Me</u>$_2$), 56.77(OMe), 61.87(C-6), 71.35(C-4), 74.48(C-3), 81.78(C-2), 84.59(C-5), 91.50 (CCl_3), 105.38(O<u>C</u>Me_2), 151.33(C-1), 166.80(N'CO). HRMS: m/z (**10b-I,II**) M^+ calcd for $C_{12}H_{19}N_2O_7Cl_3$ 408.026, found 408.026. *Anal.* Calcd for $C_{12}H_{19}N_2O_7Cl_3$ (409.60): C, 35.16; H, 4.64; N, 6.84. Found: (**10b-I,II**) C, 34.99; H, 4.73; N, 6.64.

The evaporated residue obtained by procedure B (from 0.28 g of **8b**) was partitioned between EtOAc (15 ml) and water (25 ml). The aqueous layer was lyophilized to give a pair of isomers **10-I** and **-II** as a white solid (0.12 g, 72%) identical to the product of procedure A.

N'-Methoxycarbonyl-2,5-anhydro-3,4-*O*-isopropylidene-D-allonohydrazide (10c). -Using procedure A, **8d** (0.64 g) was transformed with 0.05 M NaOMe/MeOH in 3 h into **10c**, which was isolated, by chromatography on silica gel (25 g) with CH_2Cl_2 (0.3 l) and CH_2Cl_2/MeOH (5:1) (0.15 l) and precipitation with $CHCl_3$, as a white solid (0.26 g, 65%), m.p. 168-170 °C. ^{1}H-NMR (Me_2SO-d_6) δ 1.21 and 1.45(2s, 6H, CMe_2), 3.36(s, 3H, OMe), 3.49(m, 2H, H-6a, H-6b), 4.09(m, 1H, H-5), 4.33(d, 1H, H-2), 4.66(dd, 1H, H-4), 4.77(dd, 1H, H-3), 4.97(t, 1H, OH-

6), 9.19 and 9.81(2 br s, 2H, 2 NH); $J_{2,3}$ 2.7, $J_{3,4}$ 6.0, $J_{4,5}$ 2.1, $J_{6a,OH-6}$ and $J_{6b,OH-6}$ 5.9 Hz; ^{13}C-NMR (Me_2SO-d_6) δ 25.07 and 26.95($C\underline{Me}_2$), 52.17(OMe), 61.17(C-6), 81.49(C-2), 83.51 and 83.72(C-3, C-4), 86.20(C-5), 112.55($\underline{C}Me_2$), 156.68 (C-1), 170.03(N'CO). MS: m/z 290(M^+). *Anal.* Calcd for $C_{11}H_{18}N_2O_7$ (290.27): C, 45.51; H, 6.25; N, 9.65. Found: C, 45.77; H, 6.32; N, 9.90.

2-Menthyloxy-5-(β-D-ribofuranosyl)-1,3,4-oxadiazole (11a). -Using procedure A **8c** (1.00 g) was transformed in 15 min into **11a**, which was isolated, by treatment of the evaporated residue with EtOEt and subsequent filtration in the N_2 atmosphere, as a white solid (0.34 g, 65%); m.p. 104-112 °C. ^{1}H-NMR (CD_3COCD_3) δ 0.82 and 0.92(2d, 6H, $CH\underline{Me}_2$), 0.96(m, 4H, $C\underline{H}Me$, C-4a"), 1.16(m, 2H, H-3a", H-6a"), 1.60(m, 2H, H-2", H-5"), 1.75(m, 2H, H-4b", H-3b"), 2.04(m, 1H, $C\underline{H}Me_2$), 2.33(m, 1H, H-6b"), 3.51(m, 3H, 3 OH), 3.62(dd, 1H, H-5a'), 3.71(dd, 1H, H-5b'), 4.00(q, 1H, H-4'), 4.23(t, 1H, H-3'), 4.45(t, 1H, H-2'), 4.76(m, 1H, H-1"), 4.78(d, 1H, H-1'); $J_{1',2'}$ 5.9, $J_{4',5'}$ 4.4, $J_{4',5''}$ 3.9, $J_{5',5''}$ 12.9 Hz. ^{13}C-NMR (CD_3COCD_3) δ16.57 and 20.77($CH\underline{Me}_2$), 22.10($CH\underline{Me}$), 23.83(C-2"), 26.78 ($\underline{C}HMe_2$), 31.91(C-4"), 40.40(C-6"), 48.06(C-2"), 72.22(C-3'), 74.82(C-2'), 76.76(C-1'), 85.08(C-1"), 86.60 (C-4'), 161.16 and 166.69(C-2, C-5). MS: m/z 356(M^+). *Anal.* Calcd for $C_{17}H_{28}N_2O_6$ (356.42): C, 57.29; H, 7.92; N, 7.86. Found: C, 57.08; H, 7.68; N, 8.02.

2-(2-Trichloromethyl-2-propoxy)-5-(β-D-ribofuranosyl)-1,3,4-oxadiazole (11b). A mixture of **8b** (1.00 g, 1.5 mmol) in 27% methanolic NH_3 (50 ml) was stirred at r.t. for 5 h, then concentrated and the residue treated with CH_2Cl_2 to give **11b** (0.32 g, 56%) as a white solid, m.p. 141-143 °C (water). HRMS m/z MH^+ calcd for $C_{11}H_{16}N_2O_6Cl_3$ 377.0074, found 377.0100. *Anal.* Calcd for $C_{11}H_{15}N_2O_6Cl_3$ (377.61): N, 7.42. Found N, 7.11.

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Supplementary Material Available: ^{1}H- and ^{13}C-NMR data for compounds **2g-h**, **3c-d**, **3g**, **4b-d**, **5b-d**, **6b**, **7b-d**, **8a-b**, **8d-i**, **9a-b**, and **11b** as well as six tables of proton and ^{13}C chemical shifts of 5-ribosyl-1H-tetrazoles (**2**, **4**, **5**, **6**, and **7**) and -1,3,4-oxadiazoles (**3**, **8**, **9**, **10**, and **11**)

See following pages for Supplementary Material

SUPPLEMENTARY MATERIAL

5-[2-*O*-Acetyl-3,5-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl]-1H-tetrazole (2g). ^{1}H-NMR (DMSO-d_6) δ 0.98(m, 28H, 4 i-Pr), 2.05(s, 3H, OAc), 3.41(m, 1H, H-5'), 3.69(dd, 1H, H-5"), 3.97(m, 1H, H-4'), 4.81(dd, 1H, H-3'), 5.07(d, 1H, H-1'), 5.28(dd, 1H, H-2'), 7.0(br s, 1H, NH); $J_{1',2'}$, 2.4, $J_{2',3'}$, 4.4, $J_{3',4'}$, 6.9, $J_{4',5"}$ 2.3, $J_{5',5"}$ 11.8 Hz. ^{13}C-NMR (DMSO-d_6) δ 12.63, 12.81, 13.13(4 $\underline{C}HMe_2$), 16.91, 16.97, 17.04, 17.39, 17.42, 17.45(4 $CH\underline{Me}_2$), 20.89($CO\underline{Me}$), 61.85(C-5'), 70.39(C-3'), 75.67(C-1'), 77.63(C-2'), 83.24(C-4'), 160.12(C-5), 169.79(CO).

5-[2,3-*O*-(1,1,3,3-Tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl]-1H-tetrazole (2h). ^{1}H-NMR (DMSO-d_6) δ 0.91-1.03(m, 28H, 4 i-Pr), 3.48(dd, 1H, H-5'), 3.58(dd, 1H, H-5"), 3.87-3.96(m, 2H, H-4', H-3'), 4.18(t, 1H, H-2'), 4.98(d, 1H, H-1'), 5.05, 5.30(2 br s, 2H, NH, OH-5'); $J_{1',2'}$, 5.9 Hz. ^{13}C-NMR (DMSO-d_6) δ 12.90, 17.01, 17.12, and 17.26(4 i-Pr), 61.56(C-5'), 71.04, 74.70, and 75.12(C-3', C-2', C-1'), 85.57(C-4'), 156.09(C-5).

5-[5-*O*-Benzoyl-2,3-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl)-2-methyl-1,3,4-oxadiazole (3c). ^{1}H-NMR ($CDCl_3$) δ 1.05(m, 28H, 4 i-Pr), 2.39(s, 3H, Het-Me), 4.38(dd, 1H, H-5'), 4.40(m, 1H, H-4'), 4.53(dd, 1H, H-3'), 4.67(dd, 1H, H-5"), 4.88(t, 1H, H-2'), 5.12(d, 1H, H-1'), 7.44, 7.58, 7.81(3m, 5H, Ph); $J_{1',2'}$, 4.2, $J_{2',3'}$, 4.4, $J_{3',4'}$, 5.8, $J_{4',5'}$, 4.4, $J_{4',5"}$ 4.5, $J_{5',5"}$ 13.4 Hz. ^{13}C-NMR ($CDCl_3$) δ 10.87(Het-$\underline{Me}$), 12.72, 12.81, 13.09, and 13.30(4 $\underline{C}HMe_2$), 16.96, 17.01, 17.10, 17.17, 17.21, 17.26, and 17.44(4 $CH\underline{Me}_2$), 63.85(C-5'), 74.26(C-3'), 76.06(C-2'), 76.95(C-1'), 82.41(C-4'), 128.40, 129.63, and 133.17(Ph), 164.26 and 164.66(C-2, C-5), 166.20(CO).

5-(5-*O*-t-Butyldimethylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)-2-methyl-1,3,4-oxadiazole (3d). ^{1}H-NMR ($CDCl_3$) δ -0.01 and 0.01(2s, 6H, $SiMe_2$), 0.85(s, 9H, CMe_3), 1.39 and 1.58(2s, 6H, CMe_2), 2.53(s, 3H, Het-Me), 3.64(dd, 1H, H-5'), 3.68(dd, 1H, H-5"), 4.30(m, 1H, H-4'), 4.83(dd, 1H, H-3'), 5.09(d, 1H, H-1'), 5.24(dd, 1H, H-2'); $J_{1',2'}$, 3.9, $J_{2',3'}$, 6.3, $J_{3',4'}$, 2.1, $J_{4',5'}$, 4.6, $J_{4',5"}$ 4.0 Hz. ^{13}C-NMR ($CDCl_3$) δ -5.58 and -5.56($SiMe_2$), 10.94(Het-$\underline{Me}$), 18.27($\underline{C}Me_3$), 25.30 and 27.19 ($C\underline{Me}_2$), 25.78($C\underline{Me}_3$), 63.23(C-5'), 78.16(C-1'), 82.30(C-3'), 83.34(C-2'), 86.39(C-4'), 113.99($\underline{C}Me_2$), 164.47(C-2, C-5).

5-[2-*O*-Acetyl-3,5-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl]-2-methyl-1,3,4-oxadiazole (3g). ^{1}H-NMR ($CDCl_3$) δ 0.98(m, 28H, 4 i-Pr), 2.07(s, 3H, OAc), 2.46(s, 3H, Het-Me), 3.87-3.94(m, 2H, H-5', H-4'), 4.00(dd, 1H,

H-5"), 4.54(dd, 1H, H-3'), 5.08(d, 1H, H-1'), 5.58(dd, 1H, H-2'); $J_{1',2'}$ 1.5, $J_{2',3'}$ 5.4, $J_{3',4'}$ 9.0, $J_{4',5"}$ 3.2 Hz. ^{13}C-NMR ($CDCl_3$) δ 10.93(Het-Me), 12.42, 12.72, 13.00, and 13.12(4 CHMe$_2$), 16.89, 16.94, 17.05, 17.16, 17.19, and 17.29(4 CHMe$_2$), 20.62 (COMe), 60.41(C-5'), 70.45(C-3'), 74.41(C-1'), 74.63(C-2'), 81.92(C-4'), 163.51 and 164.68(C-2, C-5), 169.43(CO).

1-Ethyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)tetrazole (4b). ^{1}H-NMR ($CDCl_3$) δ 1.52(t, 3H, CH_2Me; ^3J 7.3 Hz), 4.46(q, 2H, CH_2Me), 4.56(dd, 1H, H-5'), 4.76-4.82(m, 2H, H-4', H-5"), 5.58(d, 1H, H-1'), 6.03(t, 1H, H-3'), 6.29(t, 1H, H-2'), 7.41, 7.56, and 7.99(3m, 15H, 3 Ph); $J_{1',2'}$ 4.8, $J_{2',3'}$, $J_{3',4'}$ 5.5 Hz. ^{13}C-NMR ($CDCl_3$) δ 15.02(CH_2Me), 43.30(CH_2Me), 63.28(C-5'), 72.05(C-3'), 73.68(C-1'), 74.61(C-2'), 81.22(C-4'), 128.51, 128.83, 129.16, 129.81, 133.38, and 133.60(3 Ph), 151.22(C-5), 165.20 and 165.43(3 CO).

1-Benzyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)tetrazole (4c). ^{1}H-NMR ($CDCl_3$) δ 4.50(dd, 1H, H-5'), 4.70(m, 1H, H-4'), 4.78(dd, 1H, H-5"), 5.44(d, 1H, H-1'), 5.62 and 5.68(2d, 2H, CH_2Ph; J_{gem} 15.2 Hz), 5.95(t, 1H, H-3'), 6.32(t, 1H, H-2'), 7.26, 7.37, 7.54, 7.93(4m, 20H, 4 Ph); $J_{1',2'}$ 4.2, $J_{4',5'}$ 4.2, $J_{4',5"}$ 3.1, $J_{5',5"}$ 12.2 Hz. ^{13}C-NMR ($CDCl_3$) δ 51.43(CH_2Ph), 63.15(C-5'), 71.74(C-3'), 73.76(C-1'), 74.50 (C-2'), 80.87(C-4'), 127.71, 128.37, 128.43, 128.58, 128.61, 128.80, 128.97, 129.47, 129.65, 129.70, 133.04, 133.27, 133.54 and 133.62(4 Ph), 151.65(C-5), 165.00 and 165.85(3 CO).

1-Allyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)tetrazole (4d). ^{1}H-NMR ($CDCl_3$) δ 4.56(dd, 1H, H-5'), 4.78(dd, 1H, H-5"), 4.82(m, 1H, H-4'), 5.09(d, 2H, CH_2CH=CH_2; ^3J 5.7 Hz), 5.18(d, 1H, CH_2CH=CH-a; ^3J 17.1 Hz), 5.28(d, 1H, CH_2CH=CH-b; ^3J 10.1 Hz), 5.59(d, 1H, H-1'), 5.93(m, 1H, CH=CH_2), 6.01(t, 1H, H-3'), 6.33(t, 1H, H-2'), 7.40, 7.53, and 7.98(3m, 15H, 3 Ph); $J_{1',2'}$ 4.9 Hz. ^{13}C-NMR ($CDCl_3$) δ 49.99(NCH_2), 63.10(C-5'), 71.76(C-3), 73.54(C-1'), 74.39(C-2') 80.80(C-4'), 120.08(CH=CH_2), 129.77(CH=CH_2), 128.32, 128.37, 128.93, 129.42, 129.57, 129.62, 133.21, 133.49, and 133.60(3 Ph), 151.57(C-5), 164.99 and 165.85(3 CO).

2-Ethyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)tetrazole (5b). ^{1}H-NMR ($CDCl_3$) δ 1.57(t, 3H, CH_2Me; ^3J 7.4 Hz), 4.57(q, 2H, CH_2Me), 4.63(dd, 1H, H-5'), 4.81(m, 1H, H-4'), 4.82(dd, 1H, H-5"), 5.68(d, 1H, H-1'), 6.06(t, 1H, H-3'), 6.12(t, 1H, H-2'), 7.38, 7.55, 7.97, and 8.11(4m, 15H, 3 Ph); $J_{1',2'}$ 4.8 $J_{2',3'}$, $J_{3',4'}$, $J_{4',5'}$ 5.4, $J_{4',5"}$ 3.7, $J_{5',5"}$ 13.2 Hz. ^{13}C-NMR ($CDCl_3$) δ 14.26(CH_2Me), 48.48(CH_2Me), 63.87 (C-5'), 72.54(C-3'), 75.08(C-2'), 75.34(C-1'), 80.27(C-4'), 128.25, 128.33, 128.35,

128.81, 129.57, 129.63, 129.68, 129.73, 133.01, 133.40 and 133.43(3 Ph), 163.46(C-5), 165.05, 165.19, and 166.08(3 CO).

2-Benzyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)tetrazole (5c). ^{1}H-NMR ($CDCl_3$) δ 4.61(dd, 1H, H-5'), 4.48(m, 1H H-4'), 4.79(dd, 1H, H-5"), 5.65(d, 1H, H-1'), 5.66(s, 2H, C$\underline{H}_2$Ph), 6.05(t, 1H, H-3'), 6.11(t, 1H, H-2'), 7.37, 7.53, 7.95 and 8.10(4m, 20H, 4 Ph); $J_{1'2'}$, 5.1, $J_{4'5'}$, 5.4, $J_{5'5"}$ 12.9 Hz. ^{13}C-NMR ($CDCl_3$) δ 56.85(C$\underline{H}_2$Ph), 63.94(C-5'), 72.58(C-3'), 75.03(C-2'), 75.22(C-1'), 80.33(C-4'), 128.28, 128.34, 128.81, 128.92, 129.65, 129.68, 129.74, 132.67, 133.02, and 133.42(4 Ph), 163.77(C-5), 165.02, 165.18, and 166.09(3 CO).

2-Allyl-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)tetrazole (5d). ^{1}H-NMR ($CDCl_3$) δ 4.63(dd, 1H, H-5'), 4.82(m, 2H, H-4', H-5"), 5.12(d, 2H, C$\underline{H}_2$CH=CH$_2$; ^3J 6.2 Hz), 5.31(d, 1H, CH$_2$CH=C$\underline{H}$-a; ^3J 7.5 Hz), 5.36(s, 1H, CH$_2$CH=C$\underline{H}$-b), 5.69(d, 1H, H-1'), 6.00(m, 1H, CH$_2$C$\underline{H}$=CH$_2$), 6.06(t, 1H, H-3'), 6.13(t, 1H, H-2'), 7.37, 7.41, 7.54, 7.97, and 8.11(5m, 15H, 3 Ph); $J_{1'2'}$, 4.8, $J_{4'5'}$, 5.4, $J_{5'5"}$ 13.0 Hz. ^{13}C-NMR ($CDCl_3$) δ 55.53(NCH$_2$), 63.96(C-5'), 72.64(C-3'), 75.16(C-2'), 75.38(C-1'), 80.39(C-4'), 121.20(CH=C$\underline{H}_2$), 129.01(C$\underline{H}$=CH$_2$), 128.35, 128.43, 128.50, 128.89, 129.34, 129.72, 129.76, 129.82, 133.09, 13350, and 133.52(3 Ph), 163.79(C-5), 165.12, 165.26, and 166.15(3 CO).

1-Ethyl-5-(β-D-ribofuranosyl)tetrazole (6b). ^{1}H-NMR (DMSO-d$_6$) δ 1.43(t, 3H, CH$_2$C$\underline{H}_3$, ^3J 7.3 Hz), 3.42-3.57(m, 2H, H-5', H-5"), 3.92(m, 1H, H-4'), 4.03(m, 1H, H-3'), 4.43(t, 1H, H-2'), 4.51(q, 2H, C$\underline{H}_2$Me), 4.79(t, 1H, OH-5'), 5.04(d, 1H, H-1'), 5.14(d, 1H, OH-3'), 5.37(d, 1H, OH-2'); $J_{1'2'}$, 5.1, $J_{2'OH-2'}$, 6.2, $J_{3'OH-3'}$, 5.3, $J_{5'OH-5'}$, and $J_{5"OH-5'}$ 5.4 Hz. ^{13}C-NMR (DMSO-d$_6$) δ 15.09(Me), 42.69(C$\underline{H}_2$Me), 61.48(C-5'), 71.08(C-3'), 73.77(C-1'), 74.26(C-2'), 85.91(C-4'), 153.43(C-5).

2-Ethyl-5-(β-D-ribofuranosyl)tetrazole (7b). ^{1}H-NMR (DMSO-d$_6$) δ 1.52(t, 3H, CH$_2$C$\underline{H}_3$, ^3J 7.3 Hz), 3.46(dd, 1H, H-5'), 3.55(dd, 1H, H-5"), 3.6-4.2(br s, 3H, 3 OH), 3.89(m, 1H, H-4'), 4.03(t, 1H, H-3'), 4.30(t, 1H, H-2'), 4.71(q, 2H, C$\underline{H}_2$Me), 4.86(d, 1H, H-1'), $J_{1'2'}$, 6.2, $J_{2'3'}$, and $J_{3'4'}$, 4.8, $J_{4'5'}$, 5.5, $J_{4'5"}$ 4.5, $J_{5'5"}$ 11.4 Hz. ^{13}C-NMR (DMSO-d$_6$) δ 14.37(Me), 48.19(CH$_2$), 62.19(C-5'), 71.41(C-3'), 74.72(C-2'), 75.63(C-1'), 85.57(C-4'), 165.00(C-5).

2-Benzyl-5-(β-D-ribofuranosyl)tetrazole (7c). ^{1}H-NMR (DMSO-d$_6$) δ 3.38-3.54 (m, 2H, H-5', H-5"), 3.85(m, 1H, H-4'), 3.99(m, 1H, H-3'), 4.27(t, 1H, H-2'), 4.73(t, 1H, OH-5'), 4.86(d, 1H, H-1'), 5.07(d, 1H, OH-3'), 5.22(d, 1H, OH-2'), 5.93(s, 2H, C$\underline{H}_2$Ph), 7.38(m, 5H, Ph); $J_{1'2'}$, 6.2, $J_{2'OH-2'}$, 6.4, $J_{3'OH-3'}$, 5.3, $J_{5'OH-5'}$, and $J_{5"OH-5'}$ 5.4 Hz. ^{13}C-NMR (DMSO-d$_6$) δ 56.17(C$\underline{H}_2$Ph), 62.28(C-5'), 71.50(C-3'), 74.80(C-2'), 75.66(C-1'), 85.84(C-4'), 128.61, 128.85, 129.09, and 134.23(Ph), 165.45(C-5).

2-Allyl-5-(β-D-ribofuranosyl)tetrazole (7d). ^{1}H-NMR (DMSO-d_6, D_2O) δ 3.48 (dd, 1H, H-5'), 3.57(dd, 1H, H-5"), 3.91(m, 1H, H-4'), 4.04(t, 1H, H-3'), 4.30(m, 1H, H-2'), 4.92(d, 1H, H-1'), 5.26(md, 1H, $CH_2CH=C\underline{H}$; ^3J 10.3 Hz), 5.34(md, 2H, NCH_2; ^3J 6.1 Hz), 5.38(md, 1H, $CH_2CH=C\underline{H}$, ^3J 10.3 Hz), 6.09(tdd, 1H, $CH_2C\underline{H}=$); $J_{1',2'}$ 6.2, $J_{4',5'}$ 5.4, $J_{4',5"}$ 4.3 $J_{5',5"}$ 11.7 Hz. ^{13}C-NMR (DMSO-d_6) δ 54.86(NCH_2), 62.11(C-5'), 71.32(C-3'), 74.65(C-2'), 75.49(C-1'), 85.60(C-4'), 120.21 ($CH=\underline{C}H_2$), 130.92($\underline{C}H=CH_2$), 164.99(C-5).

2-(2,2,2-Trichloroethoxy)-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (8a). ^{1}H-NMR ($CDCl_3$) δ 4.62(m, 1H, H-5'), 4.79(m, 1H, H-4'), 4.80 (dd, 1H, H-5"), 5.03(d, 2H, CH_2CCl_3, J_{gem} 1.3 Hz), 5.43(d, 1H, H-1'), 5.97(t, 1H, H-3'), 6.06(t, 1H, H-2'), 7.40, 7.47, 7.57, 7.96, and 8.16(m, 15H, 3 Ph); $J_{1',2'}$ 6.1 Hz. ^{13}C-NMR ($CDCl_3$) δ 63.36(C-5'), 72.51(C-3'), 73.56(C-2'), 74.42(C-1'), 80.63 (OCH_2), 81.19(C-4'), 92.73(CCl_3), 128.30, 128.34, 128.41, 129.08, 129.22, 129.51, 129.61, 133.12, 133.54, and 133.58(3 Ph), 159.27 and 164.80(C-2, C-5), 165.02, 165.21, and 165.90(3 CO).

2-(2-Trichloromethyl-2-propoxy)-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (8b). ^{1}H-NMR ($CDCl_3$) δ 1.94(s, 6H, CMe_2), 4.53(dd, 1H, H-5'), 4.65(m, 1H, H-4'), 4.66(dd, 1H, H-5"), 5.23(d, 1H, H-1'), 5.84(t, 1H, H-3'), 5.94(t, 1H, H-2'), 7.29, 7.33, 7.45, 7.86, and 8.02(5m, 15H, 3 Ph); $J_{1',2'}$ 6.3 Hz. ^{13}C-NMR ($CDCl_3$) δ 20.73 and 20.83($C\underline{Me}_2$), 63.70(C-5'), 72.47(C-3'), 73.45(C-2'), 74.25(C-1'), 81.16(C-4'), 94.14($O\underline{C}Me_2CCl_3$), 104.28(CCl_3), 128.38, 128.41, 128.47, 128.62, 129.26, 129.65, 129.71, 133.18, 133.58, 133.61(3 Ph), 158.68 and 163.51(C-2, C-5), 164.91, 165.13, and 166.04(3 CO).

2-Phenyloxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (8d). ^{1}H-NMR ($CDCl_3$) δ 4.62(m, 1H, H-5'), 4.79(m, 1H, H-4'), 4.86(dd, 1H, H-5"), 5.47 (d, 1H, H-1'), 5.99(t, 1H, H-3'), 6.10(t, 1H, H-2'), 7.26(m, 5H, OPh), 7.39, 7.54, 7.96, and 8.14(4m, 15H, 3 COPh); $J_{1',2'}$ 5.9 Hz. ^{13}C-NMR ($CDCl_3$) δ 63.48(C-5'), 72.42(C-3'), 73.58(C-2'), 74.35(C-1'), 81.05(C-4'), 119.08, 126.39, 128.37, 129.30, 129.64, 129.67, 129.70, 129.80, 133.15, 133.57, and 133.60(4 Ph), 152.46 and 158.92 (C-2, C-5), 164.93, 165.13, and 166.04(3 CO).

2-Phenyloxy-5-(5-*O*-benzoyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)-1,3,4-oxadiazole (8c). ^{1}H-NMR ($CDCl_3$) δ 1.40 and 1.60(2s, 6H, CMe_2), 4.40(dd, 1H, H-5'), 4.45(dd, 1H, H-5"), 4.58(ddd, 1H, H-4'), 4.90(dd, 1H, H-3'), 5.15(d, 1H, H-1'), 5.37(dd, 1H, H-2'), 7.30, 7.42, 7.56, and 8.02(4m, 10H, 2 Ph); $J_{1',2'}$ 3.4, $J_{2',3'}$ 6.4, $J_{3',4'}$ 2.7, $J_{4',5'}$ 4.8, $J_{4',5"}$ 5.1, $J_{5',5"}$ 12.0 Hz. ^{13}C-NMR ($CDCl_3$) δ 25.30 and 27.09

($C\underline{Me}_2$), 63.95(C-5'), 77.92(C-1'), 82.21(C-3'), 82.29(C-2'), 83.96(C-4'), 114.60 ($\underline{C}Me_2$), 119.15, 126.42, 128.39, 129.40, 129.44, 129.65, and 133.19(2 Ph), 152.58(C-5), 160.11(C-2), 166.02(CO).

2-Phenyloxy-5-[5-*O*-benzoyl-2,3-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl)-1,3,4-oxadiazole (8f). ^{1}H-NMR ($CDCl_3$) δ 1.05(m, 28H, 4 i-Pr), 4.43(m, 1H, H-4'), 4.45(dd, 1H, H-5'), 4.56(t, 1H, H-3'), 4.62(dd, 1H, H-5"), 4.87(t, 1H, H-2'), 5.08(d, 1H, H-1'), 7.27-7.44, 7.53, 8.04, and 8.07(4m, 10H, 2Ph); $J_{1',2'}$, 4.4, $J_{2',3'}$, 4.6, $J_{4',5'}$, 4.4, $J_{4',5"}$ 2.7, $J_{5',5"}$ 11.5 Hz. ^{13}C-NMR ($CDCl_3$) δ 12.74, 12.82, 13.12, and 13.52(4 $\underline{C}HMe_2$), 16.96, 16.99, 17.10, 17.15, 17.21, 17.25, and 17.44(4 $CH\underline{Me}_2$), 63.95(C-5'), 74.28(C-3'), 75.77(C-2'), 77.00(C-1'), 82.55(C-4'), 119.21, 126.44, 128.40, 129.67, 129.88, and 133.12(2 Ph), 152.63 and 160.39(C-2, C-5), 166.27(CO).

2-(2-Butoxy)-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (8g). ^{1}H-NMR ($CDCl_3$) δ 0.96(t, 3H, $\underline{Me}CH$; ^3J 6.1 Hz), 1.79(m, 2H, $C\underline{H}_2Me$), 4.60(m, 1H, H-5'), 4.75(m, 1H, H-4'), 4.76(dd, 1H, H-3'), 4.94(m, 1H, $C\underline{H}MeEt$), 5.41(d, 1H, H-1'), 6.02(t, 1H, H-2'), 7.37, 7.45, 7.95, and 8.12(5m, 15H, 3 Ph); $J_{1',2'}$, 5.6 Hz. ^{13}C-NMR ($CDCl_3$) δ 9.28($CH_2\underline{Me}$), 19.90($CH\underline{Me}$), 28.56($\underline{C}H_2Me$), 63.69(C-5'), 72.48(C-3'), 73.63(C-2'), 74.57(C-1'), 80.89(C-4'), 83.25(O$\underline{C}$HMeEt), 128.47, 128.57, 128.76, 129.47, 129.74, 129.81, 133.18, and 133.61(3 Ph), 157.95 and 164.99(C-2, C-5), 165.21 and 166.16(3 CO).

2-Vinyloxy-5-[5-*O*-benzoyl-2,3-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl)-1,3,4-oxadiazole (8h). ^{1}H-NMR ($CDCl_3$) δ 1.05(m, 28H, 4 i-Pr), 4.40(m, 1H, H-4'), 4.43(dd, 1H, H-5'), 4.53(m, 1H, H-3'), 4.61(dd, 1H, H-5"), 4.79 (dd, 1H, OCH=C$\underline{H}$-a; ^3J 6.0, J_{gem} 3.0 Hz), 4.82(m, 1H, H-2'), 5.04(d, 1H, H-1'), 5.13(dd, 1H, OCH=C$\underline{H}$-b; ^3J 13.5 Hz), 7.10(dd, 1H, OC$\underline{H}$=CH_2), 7.44, 7.57, and 8.04(2tt and m, 5H, Ph); $J_{1',2'}$, and $J_{2',3'}$, 4.5, $J_{3',4'}$, 5.0, $J_{4',5'}$, 3.0, $J_{4',5"}$ 4.3, $J_{5',5"}$ 11.6 Hz. ^{13}C-NMR ($CDCl_3$) δ 12.68, 12.76, 13.07, and 13.21(4 $\underline{C}HMe_2$), 16.91, 16.95, 17.05, 17.11, 17.16, 17.21, 17.37, and 17.40(4 $CH\underline{Me}_2$), 63.79(C-5'), 74.19(C-3'), 75.77(C-2'), 76.90(C-1'), 82.54(C-4'), 100.02(=CH_2), 128.36, 129.63, and 133.10 (Ph), 144.05(OCH=), 160.36, 164.34, and 166.20(C-2, C-5, CO).

2-Vinyloxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole (8i). ^{1}H-NMR ($CDCl_3$) δ 4.60(m, 1H, H-5'), 4.76(dd, 1H, OCH=C$\underline{H}$-a; ^3J 6.0, J_{gem} 2.9 Hz), 4.77(m, 1H, H-4'), 4.79(dd, 1H, H-5"), 5.10(dd, 1H, OCH=C$\underline{H}$-b; ^3J 13.5 Hz), 5.44(d, 1H, H-1'), 5.98(t, 1H, H-3'), 6.08(t, 1H, H-2'), 7.06(dd, 1H, OC$\underline{H}$=CH_2), 7.37, 7.44, 7.53, 7.96, and 8.12(5m, 15H, 3 Ph); $J_{1',2'}$, 5.9, $J_{2',3'}$, 5.6 Hz. ^{13}C-NMR

($CDCl_3$) δ 63.31(C-5'), 72.29(C-3'), 73.46(C-2'), 74.20(C-1'), 80.89(C-4'), 99.99 ($=CH_2$), 128.27, 128.52, 129.20, 129.27, 129.53, 129.55, 129.57, 133.04, 133.46, and 133.49(3 Ph), 143.82(OCH=), 158.84 and 164.27(C-2, C-5), 164.80, 165.00, and 165.87(3 CO).

3-(2,2,2-Trichloroethyl)-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,4-oxadiazole-2(3H)-one (9a). ^{1}H-NMR ($CDCl_3$) δ 4.60(m, 1H, H-5'), 4.78(m, 2H, H-4', H-5"), 4.84(d, 2H, CH_2CCl_3, J_{gem} 7.2 Hz), 5.29(d, 1H, H-1'), 5.92(t, 1H, H-3'), 6.04 (t, 1H, H-2'), 7.35, 7.55, 7.90, 7.99, and 8.07(5m, 15H, 3Ph); $J_{1',2'}$, 4.8 Hz. ^{13}C-NMR ($CDCl_3$) δ 63.71(C-5'), 72.25(C-3'), 73.80(C-2'), 75.88(NCH_2), 80.92(C-4'), 83.42(C-1'), 99.07(CCl_3), 128.44, 128.53, 129.66, 129.71, 129.76, 133.28, 133.60, and 133.67(3 Ph), 147.32 and 161.88(C-2, C-5), 165.04, 165.27, and 166.04(3 CO<u>C</u>OPh).

3-[2-(Trichloromethyl-2-propyl)-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,3,-4-oxadiazole-2(3H)-one (9b). ^{1}H-NMR ($CDCl_3$) δ 1.91 and 1.93(2s, 6H, CMe_2), 4.54 (dd, 1H, H-5'), 4.65(m, 1H, H-4'), 4.75(dd, 1H, H-5"), 5.17(d, 1H, H-1'), 5.83(dd, 1H, H-3'), 6.08(dd, 1H, H-2'), 7.25, 7.35, 7.52, 7.80, 7.90, and 8.02(6m, 15H, 3 Ph); $J_{1',2'}$, 4.1, $J_{2',3'}$, 5.8, $J_{3',4'}$, 6.9, $J_{4',5'}$, 5.3, $J_{4',5"}$ 3.7, $J_{5',5"}$ 11.7 Hz. ^{13}C-NMR ($CDCl_3$) δ 21.10 and 21.24(C<u>Me</u>$_2$), 63.60(C-5'), 71.67(C-3'), 73.68(C-2'), 79.88(C-4'), 83.61(C-1'), 91.61(N<u>C</u>Me_2CCl_3), 104.92(CCl_3), 128.28, 128.30, 128.42, 128.62, 128.84, 129.51, 129.71, 129.81, 133.11, 133.41, and 133.53(3 Ph), 145.94 and 159.81(C-2, C-5), 164.77, 164.86, and 165.98(3 CO<u>C</u>OPh).

2-(2-Trichloromethyl-2-propoxy)-5-(β-D-ribofuranosyl)-1,3,4-oxadiazole (11b). ^{1}H-NMR (DMSO-d_6) δ 1.97 and 1.98(2s, 6H, 2 Me), 3.45(m, 2H, H-5', H-5"), 3.85(m, 1H, H-4'), 3.97(m, 1H, H-3'), 4.26(m, 1H, H-2'), 4.69(d, 1H, H-1'), 4.79(t, 1H, OH-5'), 5.14(d, 1H, OH-3'), 5.41(d, 1H, OH-2'); $J_{1',2'}$, 6.4, $J_{2',OH-2'}$, 5.5, $J_{3',OH-3'}$, 5.2, $J_{5',OH-5'}$, and $J_{5",OH-5'}$, 5.5 Hz. ^{13}C-NMR (DMSO-d_6) δ 20.69 and 20.75(C<u>Me</u>$_2$), 61.51(C-5'), 71.13(C-3'), 73.53(C-2'), 75.01(C-1'), 85.84(C-4'), 93.38(CCl_3), 104.30 ($OCMe_2$), 166.00(C-2, C-5).

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Table 1: Proton Chemical Shifts of 5-Ribosyl-1H-tetrazoles 2 and -1,3,4-oxadiazoles 3.

Compd	H-1'	H-2'	H-3'	H-4'	H-5'	H-5"	Other	Solvent[a]
2a	5.69	5.95	6.05	4.81	4.58	4.61	7.46,7.65,7.90(3Ph)	A
2b	5.41	5.26	4.98	4.60	4.27	4.34	1.36,1.55(CMe_2); 7.47,7.65,7.72(Ph)	B
2c	5.17	4.77	4.17		4.45		0.92(4Pr); 7.06,7.22,7.60(Ph)	B
2d	5.63	4.85	4.76	4.39	3.77	4.03	0.95(CMe_3); 1.36,1.60(CMe_2); 0.18,0.20($SiMe_2$); 12.7(NH)	B
2e	4.98	4.18	3.91		3.47	3.58		A
2f	4.94	4.29	4.55	——	3.86	——	0.98(4Pr); 5.3(NH,OH)	A
2g	5.35	5.58	4.70	3.94 - 4.16			1.04(4Pr); 2.08(OAc); 8.17(NH)	C
2h	4.98	4.79	4.52	3.97	3.80		0.96(4Pr); 5.35(NH,OH)	A
3a	5.52	6.07	5.98	4.77	4.58	4.88	2.37(Me); 7.39,7.47,7.58,7.96,8.12(3Ph)	B
3b	5.12	4.88	4.53	4.40	4.38	4.67	1.05(4Pr); 2.39(Me); 7.44,7.58,7.81(3Ph)	B
3c	5.09	5.24	4.83	4.30	3.64	3.68	-0.01,0.01($SiMe_2$); 0.85(CMe_3); 1.39,1.58(CMe_2); 2.53(Me)	B
3d	4.77	4.27	3.97	3.87	3.42	3.51	2.51(Me); 4.81(OH-5'); 5.16(OH-3')	B
3e	5.08	5.58	4.54	3.87-3.94		4.00	0.98(4Pr); 2.07(OAc); 2.46(Me)	A

[a] A = Me_2SO-d_6, B = $CDCl_3$, C = Me_2CO-d_6.

Table 2: Carbon-13 Chemical Shifts of 5-Ribosyl-1H-tetrazoles 2 and -2-methyl-1,3,4-oxadiazoles 3.

Compd	C-1'	C-2'	C-3'	C-4'	C-5'	Aglycon[a]	Other	Solvent[a]
2a	75.52	75.35	72.84	78.68	64.62	158.42	128.56-133.82,164.86,164.91,165.63(3Bz)	A
2b	78.67	85.02	81.68	84.77	64.98	156.20	25.28,27.16,114.86(CMe_2); 128.56-133.76, 167.26(Bz)	B
2c	80.13	76.70	74.10	81.57	64.45	160.01	12.67-17.40(4Pr); 127.31-133.15,167.64(Bz)	B
2d	78.26	85.73	80.81	86.73	64.15	156.85	-5.45($SiMe_2$); 18.49,25.93(CMe_3); 25.38,27.31,114.09(CMe_2)	B
2e	78.87	76.10	70.22	83.32	61.63	161.88		A
2f	78.14	74.92	73.47	80.48	62.79	159.15	12.08-17.35(4Pr)	A
2g	76.93	77.61	72.71	82.48	63.10	160.59	13.09-17.74(4Pr); 20.84,170.24(Ac)	C
2h	76.75	76.85	74.12	84.35	63.28	158.85	12.94-17.21(4Pr)	A
3a	74.11	73.89	72.54	81.13	63.46	162.86 164.99	10.74(Me); 128.41-133.26,165.21(3Bz)	B
3b	76.95	76.06	74.26	82.41	63.85	164.26 164.66	10.87(Me); 12.72-17.26(4Pr); 128.40-133.17,166.30(3Bz)	B
3c	78.16	83.34	82.30	86.39	63.23	164.47 164.47	-5.58,-5.56($SiMe_2$); 10.94(Me); 18.27,25.78 (CMe_3); 25.30,27.19,113.99(CMe_2)	B
3d	74.88	73.94	71.26	85.87	61.75	164.62 164.83	10.63(Me)	B
3e	74.41	74.63	70.45	81.92	60.41	163.51 164.68	10.93(Me); 12.42-17.29(4Pr); 20.62,169.43(Ac)	A

[a] A = Me_2SO-d_6, B = $CDCl_3$, C = Me_2CO-d_6.

[b] Refers to C-5 of tetrazoles 2 or to C-2 and C-5 of 1,3,4-oxadiazoles 3.

Table 3: Proton Chemical Shifts of 1- and 2-Alkyl-5-ribosyltetrazoles 4, 5, 6, and 7.

Compd	H-1'	H-2'	H-3'	H-4'	H-5'	H-5"	Other	Solvent[a]
4a	5.60	6.23	5.99	4.78-4.83		4.57	4.12(Me); 7.41,7.45,7.58,7.98(3Ph)	B
4b	5.58	6.29	6.03	4.76-4.82		4.56	1.52,4.46(Et); 7.41,7.56,7.99(3Ph)	B
4c	5.44	6.32	5.95	4.78	4.50	4.70	5.62,5.68(CH_2Ph); 7.26,7.37,7.54,7.93(4Ph)	B
4d	5.59	6.33	6.01	4.82	4.56	4.78	5.09,5.18,5.28,5.93(allyl); 7.40,7.53,7.98(3Ph)	B
5a	5.65	6.08	6.03	4.79	4.61	4.81	4.27(Me); 7.39,7.56,7.96,8.10(3Ph)	B
5b	5.68	6.12	6.06	4.81	4.63	4.82	1.57,4.57(Et); 7.38,7.55,7.97,8.11(3Ph)	B
5c	5.65	6.11	6.05	4.78	4.61	4.79	5.66(CH_2Ph); 7.37,7.53,7.95,8.10(4Ph)	B
5d	5.69	6.13	6.06	4.82		4.63	5.12,5.31,5.36,6.00(allyl); 7.37,7.41,7.54,7.97,8.11(3Ph)	B
6a	5.03	4.40	4.00	3.89	3.40-3.57		4.09(Me); 4.78(OH-5'); 5.13(OH-3'); 5.37(OH-2')	A
6b	5.04	4.43	4.03	3.92	3.42-3.57		1.34,4.51(Et); 4.79(OH-5'); 5.14(OH-3'); 5.37(OH-2')	A
7a	4.85	4.26	3.99	3.85	3.43	3.50	4.36(Me)	AD
7b	4.86	4.30	4.03	3.89	3.46	3.55	1.52,4.71(Et)	A
7c	4.86	4.27	3.99	3.85	3.38-3.54		5.93,7.38(CH_2Ph); 4.73(OH-5'); 5.07(OH-3'); 5.22(OH-2')	A
7d	4.92	4.30	4.04	3.91	3.48	3.57	5.26,5.34,5.38,6.09(allyl)	AD

[a] A = Me_2SO-d_6, AD = Me_2SO-d_6 + D_2O, B = $CDCl_3$.

Table 4: Carbon-13 Chemical Shifts[a] of 1- and 2-Alkyl-5-ribosyltetrazoles 4, 5, 6, and 7.

Compd	C-1'	C-2'	C-3'	C-4'	C-5'	C-5	Other
4a	73.55	74.34	71.91	81.17	63.21	151.71	34.31(Me); 128.45-133.70,165.14,165.16(3Bz)
4b	73.68	74.61	72.05	81.22	63.28	151.22	15.02,43.30(Et); 128.51-133.60,165.20,165.43(3Bz)
4c	73.76	74.50	71.74	80.87	63.15	151.65	51.43($\underline{C}H_2$Ph); 127.71-133.62(4Ph); 165.00,165.94(3CO)
4d	73.54	74.39	71.76	80.80	63.10	151.57	49.99,120.08,129.77(allyl); 128.32-133.60,164.99,165.85(3Bz)
5a	75.22	75.01	72.40	80.19	63.69	163.66	39.37(Me); 128.21-133.43,165.00,165.19,166.08(3Bz)
5b	75.34	75.08	72.54	80.27	63.87	163.46	14.26,48.48(Et); 128.35-133.52,165.12,165.26,166.15(3Bz)
5c	75.22	75.03	72.58	80.33	63.94	163.77	56.85($\underline{C}H_2$Ph); 128.28-133.42(4Ph); 165.02,165.18,166.09(3CO)
5d	75.38	75.16	72.64	80.39	63.96	163.79	55.53,121.20,129.01(allyl); 128.35-133.52,165.12,165.26,166.15(3Bz)
6a	74.70	74.91	71.66	86.40	62.02	154.77	35.04(Me)
6b	73.77	74.26	71.08	85.91	61.48	153.43	15.09,42.69(Et)
7a	75.43	74.67	71.36	85.56	62.13	165.04	39.50(Me)
7b	75.63	74.72	71.41	85.57	62.19	165.00	14.37,48.19(Et)
7c	75.66	74.80	71.80	85.84	62.28	165.45	56.17,128.61,128.85,129.09,134.23(CH_2Ph)
7d	75.49	74.65	71.32	85.60	62.11	164.99	54.86,120.21,130.92(allyl)

[a]Chemical shifts for 4 and 5 were determined in $CDCl_3$, for 6 and 7 were determined in Me_2SO-d_6.

Table 5: Proton Chemical Shifts[a] of Substituted 5-Ribosyl-1,3,4-oxadiazoles 8, 9, and 11.

Compd	H-1'	H-2'	H-3'	H-4'	H-5'	H-5"	Other
8a	5.43	6.06	5.97	4.79	4.62	4.80	5.03(CH_2Cl_3); 7.40,7.47,7.57,7.96,8.16(3Ph)
8b	5.23	5.94	5.84	4.65	4.53	4.66	1.94(CMe_2); 7.29,7.33,7.45,7.86,8.02(3Ph)
8c	5.43	6.04	5.95	4.75	4.63	4.79	0.94-2.35,4.79(menthyl); 7.37,7.47,7.55,7.95,8.13(3Ph)
8d	5.47	6.10	5.99	4.79	4.62	4.86	7.26,7.39,7.54,7.96,8.14(4Ph)
8e	5.15	5.37	4.90	4.58	4.40	4.45	1.40,1.60(CM_2); 7.30,7.42,7.56,8.02(2Ph)
8f	5.08	4.87	4.56	4.43	4.45	4.62	1.05(4Pr); 7.24-7.44,7.53,8.04,8.07(2Ph)
8g	5.41	6.02	5.94	4.75	4.60	4.76	0.96,1.79,4.94(2-Bu); 7.37,7.45,7.95,8.12(3Ph)
8h	5.04	4.82	4.53	4.40	4.43	4.61	1.05(4Pr); 4.79,5.13,7.10(vinyl); 7.44,7.57,8.04(Ph)
8i	5.44	6.08	5.98	4.77	4.60	4.79	4.76,5.10,7.06(vinyl); 7.37,7.44,7.53,7.96,8.12(3Ph)
9a	5.29	6.04	5.92	4.78		4.60	4.84(CH_2CCl_3); 7.35,7.55,7.90,7.99,8.07(3Ph)
9b	5.17	6.08	5.83	4.65	4.54	4.75	1.91,1.93(CMe_2); 7.25,7.35,7.52,7.80,7.90,8.02(3Ph)
9c	5.23	5.93		4.68	4.59	4.82	0.77-2.03,4.72(menthyl); 7.31-7.54,7.95,8.13(3Ph)
9d[b]	5.11	5.97	5.87	——	4.56	——	7.40,7.95(3Ph)
11a	4.78	4.45	4.23	4.00	3.62	3.71	0.82-2.33,4.76(menthyl); 3.51(3OH)
11b	4.69	4.26	3.97	3.85	3.45		1.97,1.98(CMe_2); 4.79(OH-5'); 5.14(OH-3'); 5.41(OH-2')

[a]Chemical shifts were determined in $CDCl_3$ except for 11a (Me_2CO-d_6) and 11b (Me_2SO-d_6).

[b] ^1H spectrum was recorded at 60 MHz.

Table 6: Carbon-13 Chemical Shifts[a] of Substituted 5-Ribosyl-1,3,4-oxadiazoles 8, 9, and 11.

Compd	C-1'	C-2'	C-3'	C-4'	C-5'	C-2	C-5	Other
8a	74.42	73.56	72.51	81.19	63.36	159.27	164.80	80.63,92.73(CH_2CCl_3); 128.30-133.58,165.02,165.27,165.90(3Bz)
8b	74.25	73.45	72.47	81.16	63.70	158.68	163.51	20.73,20.83,104.28(CMe_2CCl_3); 123.38-133.61,164.91,165.13,166.04(3Bz)
8c	74.40	72.70	72.41	80.69	63.61	157.82	166.06[b]	16.16-47.24,84.90(menthyl); 128.36-133.56,164.89[b],165.10[b],166.10[b](3Bz)
8d	74.35	73.58	72.42	81.05	63.48	152.46	158.92	119.08-133.60(4Ph); 164.93,165.13,166.04(3CO)
8e	77.92	82.29	82.21	83.96	63.95	152.58	160.11	25.30,27.09,114.60(CMe_2); 119.21-133.12(2Ph); 166.02(CO)
8f	77.00	75.77	74.28	82.55	63.95	157.95	160.39	12.74-17.44(4Pr); 119.21-133.12(2Ph); 166.27(CO)
8g	74.57	73.63	72.48	80.89	63.69	157.95	164.99[b]	9.28,19.90,28.56,83.25(Bu); 128.47-133.61,165.21[b],166.16[b](3Bz)
8h	76.90	75.77	74.19	82.54	63.79	160.36	164.34	12.68-17.40(4Pr); 100.02,144.05(vinyl); 128.36,129.63,133.10,166.20(Bz)
8i	74.20	73.46	72.29	80.89	63.31	158.84	164.27[b]	99.99,143.82(vinyl); 128.27-133.49,164.80[b],165.00[b],165.87[b](3Bz)
9a	83.42	73.80	72.25	80.92	63.71	147.32	161.88	75.88,99.07(CH_2CCl_3); 128.44-133.67,165.04,165.27,166.04(3Bz)
9b	83.61	73.68	71.67	79.88	63.60	145.94	159.81	21.10,21.24,91.61,104.92(CMe_2CCl_3); 128.28-133.53,164.77,164.86,165.98(3Bz)
9c	82.50	72.70	72.41	80.69	63.61	151.86	164.78[b]	16.12-46.86,76.53(menthyl); 128.20-133.50,164.85[b],165.00[b],165.81[b](3Bz)
9d[c]	75.16[b]	73.10[b]	72.34[b]	80.58	63.46	153.39	154.37	126.39-133.56,164.98,166.17(3Bz)
11a	76.76	74.82	72.22	86.60	62.68	161.16	166.69	16.57-48.06,85.08(menthyl)
11b	75.01	73.53	71.13	85.84	61.51	166.00		20.69,20.75,93.38,104.30(CMe_2CCl_3)

[a]Chemical shifts were determined in $CDCl_3$ except for 11a (Me_2CO-d_6) and 11b (Me_2SO-d_6).

[b]Tentative assignements. [c] ^{13}C spectrum was recorded at 22.50 MHz.