239. Aldonhydroximo-lactones. Preparation and Determination of Configuration

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The syntheses of the unprotected, (*Z*)-configurated hexon- and pentonhydroximo-lactones **2a**–**12a** by oxidation of D-glucose, cellobiose, D-galactose, D-mannose, 2-acetamido-2-deoxy-D-glucose, D-ribose, and D-arabinose oxime with MnO_2, $Hg(OAc)_2$, or O_2 in the presence of Cu_2Cl_2/pyridine are described. An (*E*/*Z*)-pair of protected hydroximo-lactones **14** and **15** was obtained by oxidation of the diisopropylidene-D-mannose oxime **13** with MnO_2. In CH_2Cl_2 solution, the minor (*E*)-isomer **15** was slowly transformed into the major (*Z*)-isomer **14**. The structure assignments for **2a**–**12a** are based upon IR and NMR data, the *Beckmann* rearrangement of **1** and **14**, and the X-ray structure analysis of **7a** and **47**. From the selectively deprotected hydroximo-lactones **2c**, **8c**, and **9c**, the urethanes **2d**, **2f**, **8d**, and **9d** were prepared. (*E*/*Z*)-mixtures of the amino phosphates **27**/**28**, **29**/**30**, and **31**/**32** were obtained from the bromonitroso ethers **16**, **19**, and **17** and $NaPO(OEt)_2$. The configuration of the bromonitroso ethers **18** and **19** were assigned on the basis of their CD spectra and of their correlation with the corresponding bromonitro ethers **24** and **25**. Factors influencing the configuration of the hydroximo-lactones are briefly discussed.

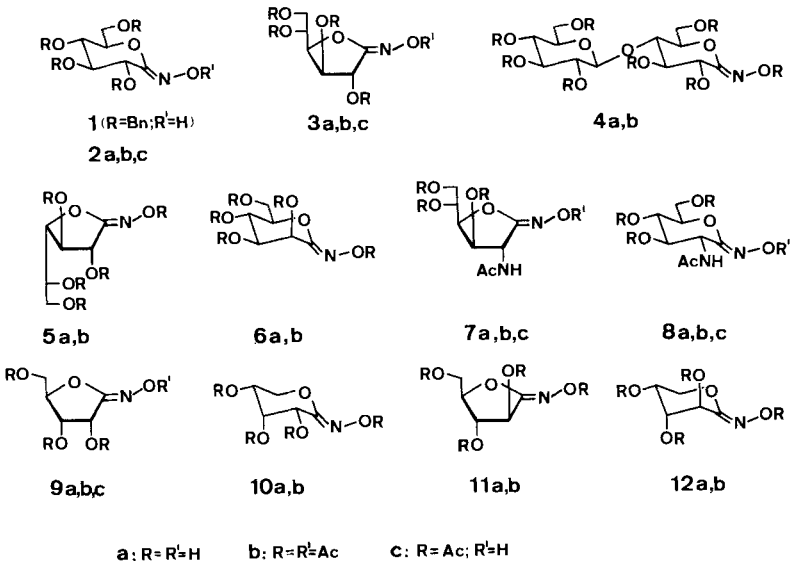
Introduction. – Protected aldonhydroximo-lactones ('aldonolactone oximes') have been prepared as intermediates in the synthesis of halonitroso and halonitro ethers [1]. Based on the lack of reactivity of these protected hydroximo-lactones under standard conditions for *Beckmann* rearrangement and considering the greater stability of (*E*)-configurated acyclic analogues, they have tentatively been assigned the (*E*)-configuration [2].

Unprotected aldonhydroximo-lactones are analogues of aldonolactones and may thus be competitive β-glycosidase inhibitors [3] [4]. Modifications of the *N*-hydroxy group of hydroximo-lactones may lead to stronger or to irreversible inhibitors and to ligands for affinity chromatography [5]. Unlike the aldono-1,5-lactones, the corresponding hydroximo-lactones are expected to resist hydrolysis under physiological conditions.

Attempts to deprotect the 2,3,4,6-tetra-*O*-benzyl-D-gluconhydroximo-lactone **1** failed, but a synthesis of free hydroximo-lactones directly from aldose oximes appeared both attractive in view of a 'minimal protection strategy' in carbohydrate synthesis (*cf.* [6–10]) and feasible, since aldoximes exist in equilibrium with cyclic hydroxylamines [11–14]. Mild oxidation conditions should selectively lead to hydroximo-lactones.

Preparation of Hydroximo-lactones. – The oximes of D-glucose, cellobiose, D-mannose, D-galactose, 2-acetamido-2-deoxy-D-glucose, D-ribose and D-arabinose were oxidized by activated MnO_2 [15], by $Hg(OAc)_2$ in the presence of Na_2CO_3, or by O_2 in the presence of Cu_2Cl_2 and pyridine [16]. The structure and the yield of the resulting hydroximo-lactones depend both on the starting material and on the method of oxidation[1]).

[1]) Attempts to oxidize the aldoximes with Br_2 or with O_2 in the presence of noble-metal catalysts did not give useful yields of hydroximo-lactones.



Thus, D-glucose oxime gave a single, crystalline hydroximo-1,5-lactone **2a**[2]) by oxidation with MnO_2, the amorphous hydroximo-1,4-lactone **3a**[2]) upon oxidation with O_2/Cu_2Cl_2/pyridine, and a mixture **2a**/**3a** in the presence of $Hg(OAc)_2$. From cellobiose oxime, the cellobionhydroximo-1,5-lactone (**4a**) was obtained in moderate yields together with products of glycoside cleavage. D-Galactose oxime gave a single hydroximo-1,4-lactone

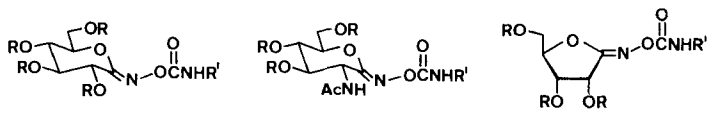
Table. *C=N Stretching Vibrations in the IR Spectra and C(1) Chemical Shifts in the ^{13}C-NMR Spectra of Hydroximo-lactones*

Hydroximo-1,5-lactone	$\tilde{\nu}$(C=N) [cm^{-1}]	δ(C(1)) [ppm]	Hydroximo-1,4-lactone	$\tilde{\nu}$(C=N) [cm^{-1}]	δ(C(1)) [ppm]
Unprotected compounds					
2a	1678	156.1	**3a**	1695	161.0
4a	1672	154.7			
			5a	1693	158.7
6a	1680	156.4			
8a	1658	153.1	**7a**	1705	158.3
			9a	1699	160.5
			11a	1691	159.8
Protected compounds					
2b	1663	153.5	**3b**	1686	158.9
4b	1665	153.8			
			5b	1684	159.0
6b	1656	153.8			
8b	1643	158.1	**7b**	1678	161.9
10b	1652	153.8	**9b**	1686	158.7
12b	1652	155.0	**11b**	1682	159.3

[2]) The C=N stretching vibrations in the IR spectra of the hydroximo-lactones and the C(1) chemical shifts in their ^{13}C-NMR spectra depend on the ring size, in an analogous way as it is known for carbonyl compounds (*Table 1*).

5a. D-Mannose oxime was difficult to oxidize. It gave a low yield of **6a**, which decomposed partially under the reaction conditions. 2-Acetamido-2-deoxy-D-glucose oxime gave mixtures of the crystalline hydroximo-1,4-lactone **7a** and the amorphous hydroximo-1,5-lactone **8a**, which were easily separated by crystallization. From D-ribose oxime, mainly the hydroximo-1,4-lactone **9a** was obtained together with some **10a**. Under the same conditions, D-arabinose oxime gave the crystalline hydroximo-1,4-lactone **11a** and the unstable hydroximo-1,5-lactone **12a**. All these hydroximo-lactones decompose in the presence of aqueous acids.

Acetylation of the hydroximo-lactones gave the stable peracetates **2b**–**12b**, which upon deacetylation with NH_3/MeOH regenerated the unprotected products in almost quantitative yields. Selective deacetylation of **2b**, **3b**, **7b**, **8b**, and **9b** in MeOH and in the presence of 1 mol-equiv. of $MeNH_2$ gave the glucose derivatives **2c** and **3c**, the *N*-acetylglucosamine derivatives **7c** and **8c**, and the ribose derivative **9c**, respectively, in fair yields. Addition of methyl isocyanate in the presence of Et_3N to **2c**, **8c**, and **9c** generated the methylurethanes **2d**, **8d**, and **9d**, respectively. Similarly, the phenylurethane **2f** was obtained from **2c** and phenyl isocyanate. The deprotected urethanes **2e**, **2g**, **8e**, and **9e** were obtained in high yields by standard deacetylation.



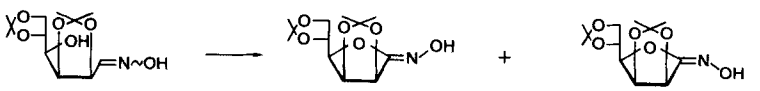
2d,e,f,g **8d,e** **9d,e**

d: R=Ac; R'=CH_3 **e**: R=H; R'=CH_3 **f**: R=Ac; R'=C_6H_5 **g**: R=H; R'=C_6H_5

Determination of Configuration. – In all cases, oxidation of the unprotected aldoximes gave the hydroximo-lactones as single diastereoisomers. Both diastereoisomers of acyclic hydroximates (='ester oximes') have been obtained by UV-induced or by acid-catalysed isomerization and their structure have been established by X-ray analysis and by NMR spectroscopy [17] [18]. Acids or UV-irradiation, however, destroyed the aldon-hydroximo-lactones.

Of the protected aldoximes, only diisopropylidenemannose oxime **13** gave (MnO_2, r.t.) two hydroximo-lactones *(Scheme 1)*. The higher-melting isomer, obtained as the major product, was identical with **14** [2]. On heating or standing in CH_2Cl_2 solution, the lower-melting compound **15** isomerized to **14**.

Scheme 1

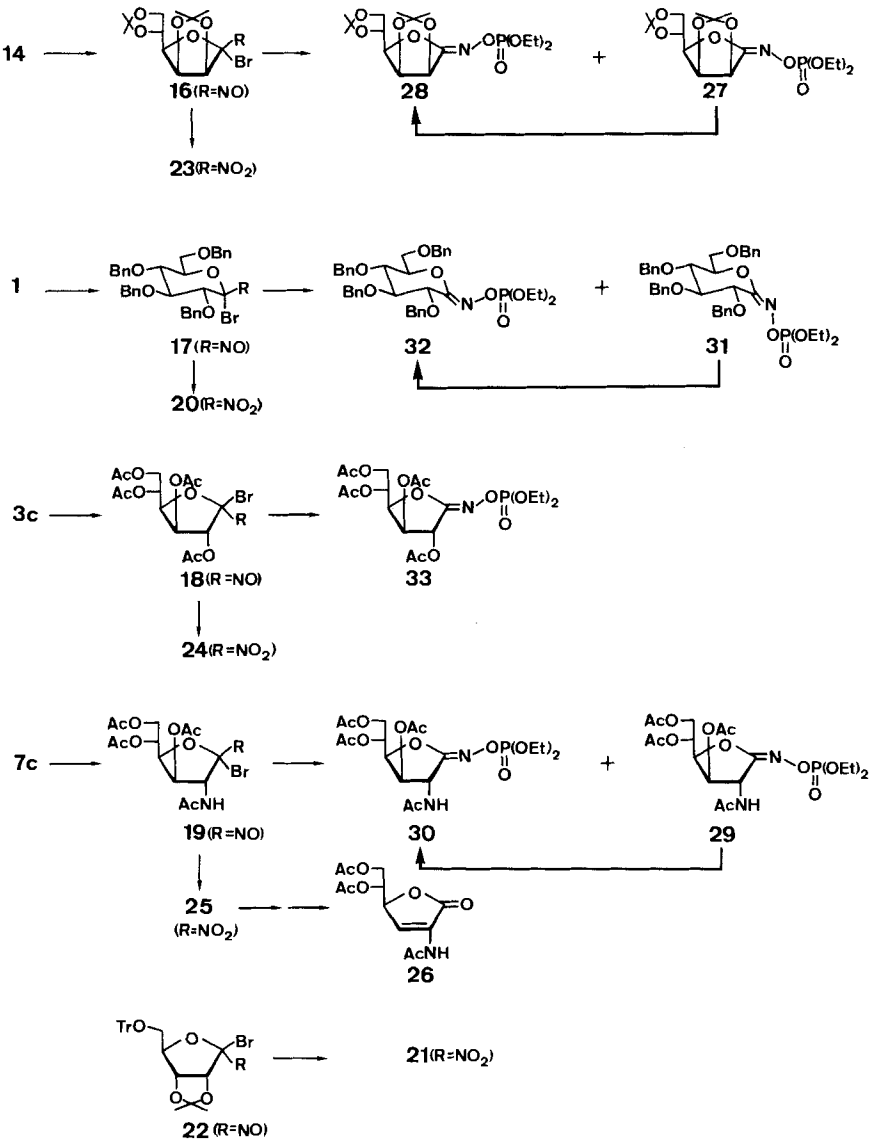


13 **14** **15**

In the ^{1}H-NMR spectra, H–C(2) of **14** appeared at 5.19 ppm, that of **15** at 5.49 ppm. Deshielding is expected for the (*E*)-isomer, in which the OH group is closer to H–C(2). The ^{13}C-NMR spectra showed C(1) resonances for **14** and **15** at 156.1 and 164.5 ppm, respectively. These shift values are in good agreement with those observed for (*E*/*Z*)-pairs of alkyl acetohydroximates [17].

To obtain additional pairs of diastereoisomeric hydroximo-lactones, we examined their preparation starting with the corresponding α-bromo-α-nitroso ethers. Treatment of such ethers with dialkylphosphite anions yields *O*-glycosylideneamino phosphates (='lactone-oxime phosphates') as mixtures of diastereoisomers [19] which might be hydrolysed to give the corresponding hydroximo-lactones *(Scheme 2)*. The bromonitroso ethers **16** and **17** have been prepared before [1]. Similarly, the diastereoisomerically pure **18** and **19** were obtained by treating **3c** and **7c**, respectively, with *N*-bromosuccini-

Scheme 2



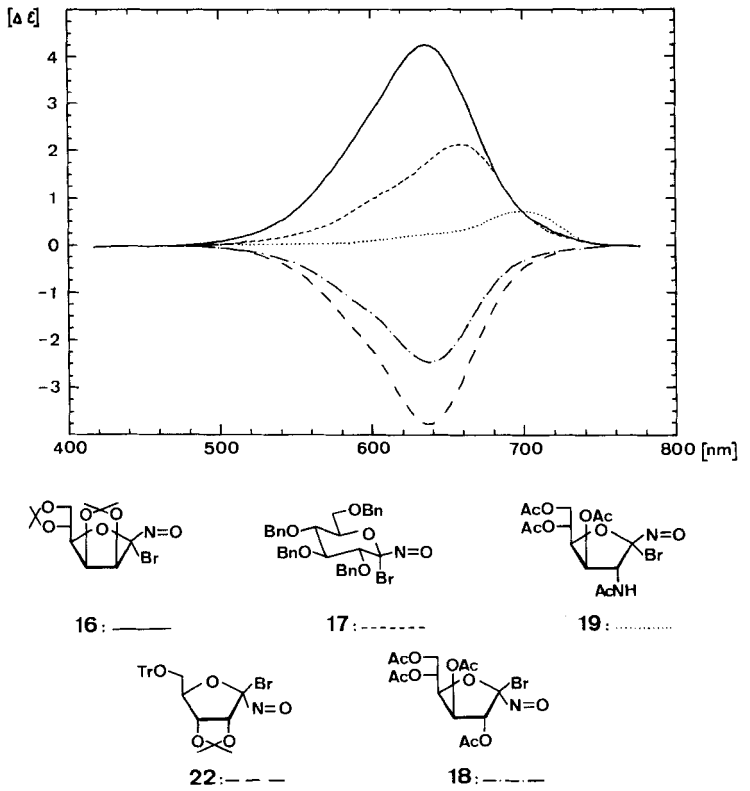


Fig. 1. *CD spectra of* **16**–**19** *and* **22**

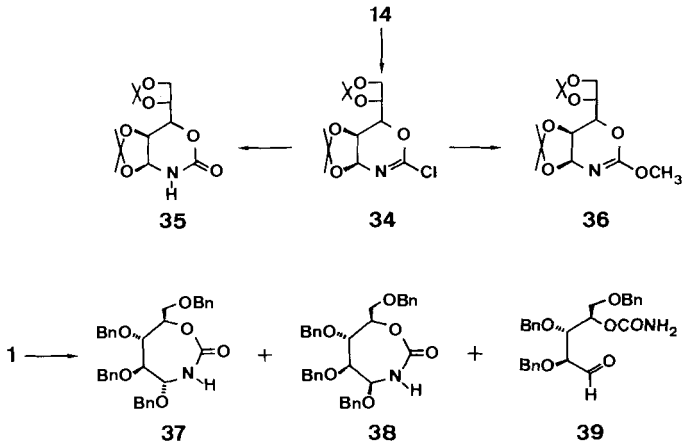
mide (NBS) und NaOAc. The configuration of the bromonitro ethers **20** and **21**, corresponding to the bromonitroso ethers **17** and **22** has been assigned on the basis of a comparison of their specific rotations with the one of **23** (corresponding to **16**), the structure of which was established by an X-ray analysis [1]. Oxidation of **18** gave the bromonitro ether **24**, to which the (1*R*)-configuration was assigned[3]). Oxidation of **19** gave the crystalline bromonitro ether **25**, which rapidly decomposed to the α,β-unsaturated lactone **26**. The CD spectra of the bromonitroso ethers *(Fig. 1)* are in agreement with these configurational assignments and indicate the (1*S*)-configuration for **19**.

Upon treatment with sodium diethyl phosphite, **16**, **19**, and **17** gave mixtures of the amino diethyl phosphates **27**/**28**, **29**/**30**, and **31**/**32**, respectively. The bromonitroso ether **18** gave a single isomer **33**. The easy isomerization of the minor isomers to the major ones did not permit their isolation. The ^{1}H- and ^{13}C-NMR spectra of the mixtures showed clearly separated sets of signals for H–C(2) and C(1)[4]), respectively, with the signals of the unstable products appearing at lower field. Hence, the major isomers were assigned

[3]) $[M]_D = -453°$; for the *B* value compare [20] [21].

[4]) The coupling constants ^3J(C(1),P) of the (*E*)- and the (*Z*)-configurated compounds were *ca.* 18 and 12 Hz, respectively.

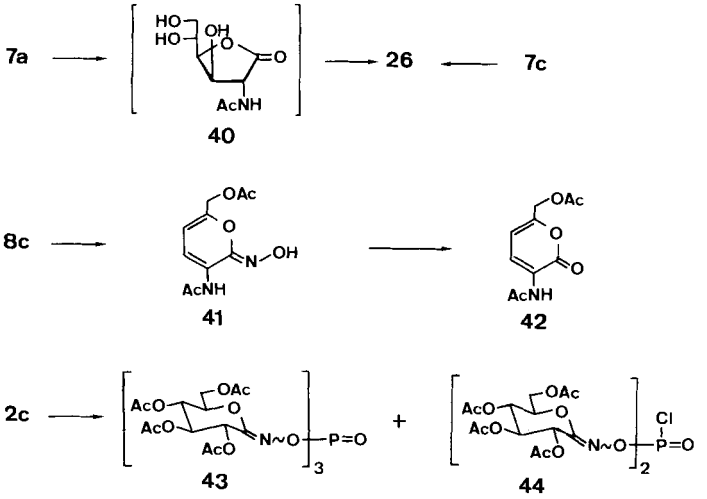
Scheme 3



the (*Z*)-configuration. Treatment of the (*E*/*Z*)-mixture **27**/**28** with NaOMe in MeOH lead only to the stable hydroximo-lactone **14**, which was again phosphorylated [22] to give exclusively the phosphate **28**[5]).

As a further piece of evidence, *Beckmann* rearrangement [18] of the lactone oximes were (re)examined (*cf.* [2]). Treatment of **14** with BuLi (1 equiv.), followed by PCl_5 in CH_2Cl_2 at 0° gave immediately the chlorodihydrooxazine **34** (*Scheme 3*)[6]) which decom-

Scheme 4

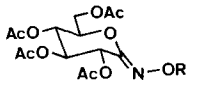


[5]) After similar treatment of the (*E*)-hydroximo-lactone **15**, a 44:56 mixture **27**/**28** was isolated.

[6]) The IR spectrum of crude **34** showed a strong absorption at 1663 cm^{-1}.

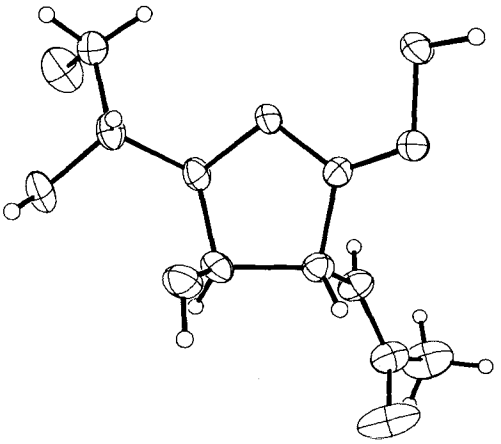
posed upon removal of the solvent. Acid hydrolysis of **34** gave the urethane **35**, whilst treatment of **34** with NaOMe in MeOH gave the iminocarbonate **36**. The reaction of **1** with PCl_5 gave a mixture of urethanes **37** and **38** and the carbamoyl-arabinose **39** in a total yield of 39%[7]).

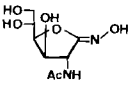
The acylated hydroximo-lactones did not undergo a *Beckmann* rearrangement (*Scheme 4*). Thus, heating of **7a** in DMSO containing 1 equiv. of TsOH gave the labile lactone **40**. Acetylation of **40** afforded the α,β-unsaturated lactone **26**, which was also obtained by treating the partially deprotected **7c** either with DMSO/TsOH or with PCl_5 in CH_2Cl_2. Similarly, the partially deprotected **8c** gave a mixture of the 2-pyrone oxime **41** and the 2-pyrone **42**, the latter being the final product of the reaction. Treatment of partially deprotected **2c** with PCl_5 in CH_2Cl_2 afforded the phosphates **43** and **44**; no rearrangement product could be isolated. The mesylate **45** and the triflate **46** decomposed slowly when heated with Et_3N or pyridine (EtOH or dioxane solution) or when heated in DMSO in the presence of TsOH[8]).



45 R=SO_2CH_3 **46** R=SO_2CF_3

Taken together, all evidence points to the (*Z*)-configuration of the thermodynamically preferred diastereoisomers of these hydroximo-lactones. For the hydroximo-lactones **7a** and **47**, the (*Z*)-configuration was established by X-ray analysis (*Fig. 2* and *3*)[9]).





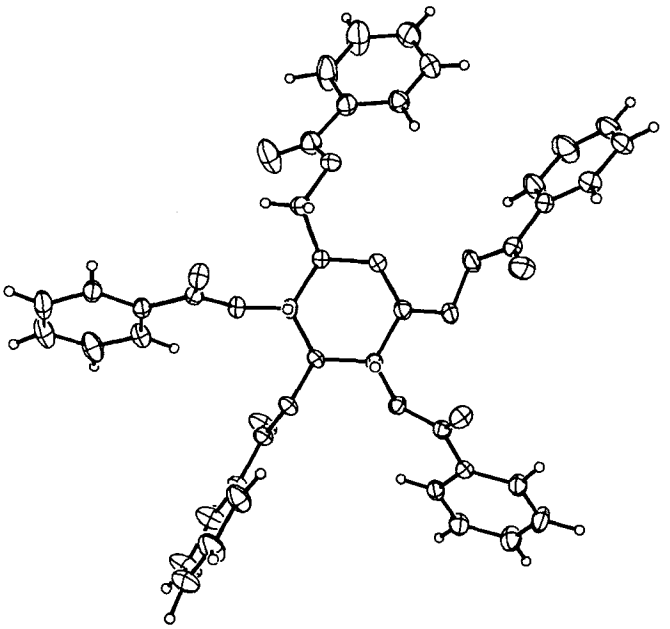
7a

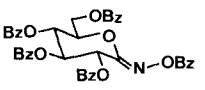
Fig. 2. *Stereoview of the hydroximo-lactone* **7a**

[7]) Shaking a solution of **37** in CH_2Cl_2 with PCl_5 and H_2O gave **38**/**39**. The *Beckmann* type 1 rearrangement of **1** leads presumably to **37**, which isomerised to **38** and hydrolyzed to **39** under workup conditions.

[8]) For the behaviour of tosylated thiohydroximates, see [23].

[9]) The X-ray analyses were performed in our institute by Dr. *R. Prewo*, from whom the crystallographic data may be obtained.





47

Fig. 3. *Stereoview of the hydroximo-lactone* **47**

Discussion. – In contrast to acyclic hydroximates (='ester oximes'), where the (*E*)-isomers are thermodynamically preferred [17] [18] [24–26], hydroximo-lactones exist preferentially as (*Z*)-isomers (*cf.* [27]). The preference for the (*Z*)-configuration is not due to a H-bond between O*H* and C(1)–*O* [25], but may be correlated with an $n_N,\sigma^*C(1)-O$ hyperconjugation, absent in the (*E*)-isomer.

The preference of acyclic hydroximates [25] for the (*E*)-configuration parallels the one of esters [28] [29]. The higher stability of (*E*)-configurated acyclic hydroximates may be due to steric interactions [30]. Analysis of the available results showed no significant correlation of configuration and bond length.

We thank the *Swiss National Science Foundation* and *Sandoz AG*, Basel for generous support and Dr. *R. Prewo* for the X-ray analyses.

Experimental Part

1. *General.* All solvents were distilled before use; H_2O was distilled twice. All reagents were obtained from *Fluka* (*purum* or *puriss. p. A.*); activated MnO_2 was prepared following [15]. Normal workup refers to [31]; solns. were evaporated at or below 40° in a *Büchi* rotary evaporator. TLC: *Merck* precoated silica gel *60 F-254* plates; detection by spraying with a 0.025M I_2 soln. in 10% aq. H_2SO_4, followed by heating at about 200°. Column chromatography: silica gel *Merck 60* (flash chromatography (FC): 40–63μ; medium-pressure chromatography (MPLC) [32]: 15–40μ) with redistilled solvents. Solvent mixtures: *A* = AcOEt/MeOH/H_2O 7:2:1, *B* = AcOEt/MeOH/H_2O 65:23:12, *C* = AcOEt/hexane 3:2, *D* = AcOEt/hexane 7:3, *E* = AcOEt/dimethoxyethane 6:1, *F* = AcOEt/hexane 1:1, *G* = AcOEt/hexane 2:1, *H* = AcOEt/MeOH 19:1, *I* = AcOEt/hexane 17:3, *K* = AcOEt/MeOH/H_2O 85:12:3, *L* = $CHCl_3$/EtOH 25:1, *M* = AcOEt/toluene 1:1, *N* = toluene/EtOH 93:7, *O* = AcOEt/hexane 4:1, *P* = MeCN/H_2O 17:3, *Q* = dimethoxyethane/hexane 1:4, *R* = AcOEt/MeOH/H_2O 45:4:1, *S* = dimethoxyethane/toluene 1:9, *T* = AcOEt/MeOH/H_2O 28:4:1, *U* = dimethoxyethane/toluene 3:17,

V = AcOEt/toluene 2:1. M.p. (uncorrected): *Büchi-510* apparatus. Optical rotations: *Perkin-Elmer-241* polarimeter, 1-dm cell, at 365, 436, 546, 578, and 589 nm; the specific rotation at 589 nm was determined using a regression curve. UV: unless otherwise stated, *Perkin-Elmer-555* spectrophotometer; CH_2Cl_2 solns. CD: *JASCO-J-500-A* spectropolarimeter; CH_2Cl_2 solns. at r.t. IR: unless otherwise stated, 3% $CHCl_3$ solns.; *Perkin-Elmer-298* spectrometer. ^{1}H-NMR and ^{13}C-NMR: *Varian-FT-80* (^{1}H(80 MHz)), *Varian-HA-100* (^{13}C(25.2 MHz)), *Varian-XL-200* (^{1}H(200 MHz), ^{13}C(50.4 MHz)), or *Bruker-AM-400* spectrometer (^{1}H(400 MHz), ^{13}C(100.6 MHz)); chemical shifts refer to TMS or 3-trimethylsilyl-1-propanesodium sulfonate as internal standard. MS: *Varian-711* apparatus (EI and FAB) or *Varian-112* apparatus (CI). Microanalysis: *FR-84 CHN* analyser.

2. *General Methods.* 2.1. *Preparation of the Aldoximes*[10]. A hot soln. of NaOEt, prepared from Na (27.6 g, 1.2 mol) in EtOH (600 ml), was added to a vigorously stirred soln. of powdered hydroxylammonium chloride (90.3 g, 1.3 mol) in EtOH (1100 ml). The mixture was cooled in ice and filtered. The filtrate (pH $\approx$ 7) was heated to 50°, and the aldose (1 mol) was added in small portions with stirring. When TLC (*A*) indicated the disappearance of the aldose, the mixture was concentrated[11]), and the oxime was crystallized from the indicated solvent.

2.2. *Oxidation of the Unprotected Aldoximes.* 2.2.1. *With MnO_2.* Activated MnO_2 (9.70 g, 2 equiv.) and the aldoxime (50 mmol) were added to a stirred soln. of KH_2PO_4 (17.20 g) and NaOH (2.94 g) in 1 l of H_2O. When the reaction was over, the mixture was filtered through *Celite* and the filtrate was concentrated *i.v.* at r.t. to 50 ml. MPLC (500 g; *A*)[12]) of the residue afforded the hydroximo-lactones, which were used for synthesis whithout further treatment.

2.2.2. *With $Hg(OAc)_2$.* To a stirred soln. of the aldoxime (1 mmol) in MeOH (10 ml) were added, at 50°, Na_2CO_3 (530 mg, 5 mmol) and $Hg(OAc)_2$ (637 mg, 2 mmol). The mixture was stirred overnight at 50°, filtered through *Celite*, and the filtrate was evaporated to dryness. The residue was acetylated (see below).

2.2.3. *With O_2.* A *Teflon*-coated autoclave (*Berghoff*) was charged with a soln. of Cu_2Cl_2 (40 mg, 0.4 mmol) in pyridine (10 ml) and a soln. of the aldoxime (1 mmol) in MeOH and pyridine (10 ml each). The mixture was stirred at r.t. under O_2 (10 bar) for the indicated period of time. The volatile material was distilled off *i.v.*, the residue suspended in H_2O and filtered through a pad of *Celite*. Ion-exchange chromatography (10 cm^3 of *Amberlite MB-3*) of the filtrate afforded colourless eluates, which were lyophilized.

2.3. *Acetylation of the Hydroximo-lactones.* Under cooling, Ac_2O (10 ml) was added dropwise to a soln. of the hydroximo-lactone (1 mmol) in pyridine (30 ml). The mixture was allowed to warm to r.t. After completion of the reaction, the mixture was evaporated to dryness under high vacuum and the residue was worked up as usual (CH_2Cl_2/1M $NaHCO_3$). The crude product was purified as indicated.

2.4. *Selective Deacetylation of the Peracetylated Hydroximo-lactone.* To an ice cold soln. of the peracetylated hydroximo-lactone (1 mmol) in MeOH (30 ml) was added dropwise, over 20 min, a CH_3NH_2 soln. (0.08M in EtOH, 12.4 ml; 1 ml 33% soln. in EtOH was diluted to 100 ml). The mixture was immediately concentrated in a rotary evaporator at r.t. and flash-chromatographed (40 g/solvent).

2.5. *Deacetylation of the Acetylated Hydroximo-lactone.* To an ice cold soln. of the acetylated hydroximo-lactone (1 mmol) in MeOH (20 ml), sat. NH_3/MeOH (10 ml, *ca.* 4M) was added. After completion of the reaction, the mixture was evaporated. MPLC (20 g, *A*[13])) of the residue afforded hydroximo-lactones, which were directly used.

2.6. *Preparation of the Glycosylideneamino Carbamates.* To a stirred soln. of the selectively deacetylated hydroximo-lactone (1 mmol) in THF (10 ml) was added Et_3N (0.7 ml, 5 mmol) and the isocyanate (2 mmol). When TLC showed complete reaction, the mixture was concentrated *i.v.* and flash-chromatographed (50 g, *C*[14])). The products were deacetylated as indicated above, and the products were purified by MPLC (20 g, *A*[15])).

2.7. *Preparation of the Bromonitroso Ethers.* A suspension of NaOAc (117 mg, 1.4 mmol) and NBS (279 mg, 1.5 mmol) in H_2O (3 ml) was added to an ice-cold stirred soln. of the selectively deacetylated hydroximo-lactone (1 mmol) in CH_2Cl_2 (4 ml)[16]). After disappearance of the starting material (TLC), the mixture was worked up as usual (CH_2Cl_2). The crude, intensely blue residue was directly used.

2.8. *Preparation of the (E/Z)-(D-Glycosylidene)amino Diethyl Phosphates.* A soln. of the crude bromonitroso ether in THF (10 ml) was cooled to −78° and treated with a soln. of NaH (79 mg, 3.3 mmol) and diethyl phosphite

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[10]) *Cf.* [33–39].

[11]) Except in the case of D-mannose oxime which could be directly filtered from the mixture.

[12]) For **4a**, solvent system *B* was used.

[13]) For **4b**, solvent system *B* was used.

[14]) For **8d**, solvent system *H* was used.

[15]) For **2g**, solvent system *K* was used.

[16]) In the case of **3c**, one crystal of Bu_4NHSO_4 had to be added.

(450 µl) in THF (10 ml) until the blue colour disappeared. Evaporation of the mixture, usual workup (CH_2Cl_2) and flash filtration (25 g/solvent) afforded the phosphates as syrups.

2.9. *Preparation of the Bromonitro Ethers.* A soln. of the crude bromonitroso compound (*ca.* 1 mmol) in CH_2Cl_2 (5 ml) was cooled to −78° and treated with O_3 until the blue colour disappeared and the mixture became pale violet. After purging with N_2, the mixture was warmed to r.t. Evaporation afforded the crude bromonitro ethers, which were purified as described below.

3. *2-Acetamido-2-deoxy-*D*-glucose Oxime.* Following *2.1*, 170.1 g (72%) of the oxime were obtained[17]). $R_f(P)$ 0.39; m.p. 99–103° (dec., MeOH/MeCN); $[\alpha]_D^{25} = +13.0°$ (*t* = 5 min, *c* = 1, H_2O); $[\alpha]_D^{25} = +9.9°$ (*t* = 50 min, *c* = 1, H_2O). IR (KBr): 3470*s*, 3430 (sh), 3400 (br.), 3285*s*, 3220 (sh), 3060 (sh), 2990*w*, 2960*m*, 2940*m*, 2890*m*, 2810*w*, 2750 (br.), 1640*s*, 1550*s*, 1465 (sh), 1440 (br.), 1395 (sh), 1388*m*, 1372*m*, 1350*m*, 1301*m*, 1278*m*, 1255*w*, 1230*w*, 1209*m*, 1143*m*, 1210*s*, 1192*s*, 1036*s*, 1032*s*, 1011*w*, 969*m*, 950*m*, 939*s*, 928*s*, 882*s*, 830 (br.), 711 (br.), 662*s*, 625*m*. ^{1}H-NMR (400 MHz, D_2O): 7.50 (*d*, *J* = 6.1, H–C(1)); 4.72 (*dd*, *J* = 7.3, 6.1, H–C(2)); 4.10 (*dd*, *J* = 7.3, 1.8, H–C(3)); 3.85, 3.65 (*J* = 11.8, 6.3, 2.9, H–C(6), H–C(6′)); 3.76 (*ddd*, *J* = 8.5, 6.3, 2.9, H–C(5)); 3.57 (*dd*, *J* = 8.5, 1.8, H–C(4)). ^{13}C-NMR (50.4 MHz, (D_6)DMSO, *t* = 10.5 min): 169.5 (*s*, CH_3CO); 148.7 (*d*, C(1)); 71.5, 70.6, 69.9 (3*d*); 63,5 (*t*, C(6)); 51.8 (*d*, C(2)); 23.0 (*q*, CH_3). ^{13}C-NMR (50.4 MHz, D_2O, *t* = 24 h): 177.2 (*s*); 176.5 (*s*); 152.1 (*d*); 151.7 (*d*); 91.9 (*d*); 79.6 (*d*); 77.0 (*d*); 73.4 (*d*); 73.1 (*d*); 72.5 (*d*); 72.4 (*d*); 71.8 (*d*); 71.3 (*d*); 65.3 (*t*); 63.4 (*t*); 54.4 (*d*); 50.6 (*d*); 24.9 (*q*); 24.6 (*q*). FAB-MS: 237 ($M^+ + 1$). Anal. calc. for $C_8H_{16}N_2O_6$ (236.224): C 40.68, H 6.83, N 11.86; found: C 40.78, H 6.70, N 11.70.

Cellobiose Oxime. Following *2.1*, 289.4 g (81%) of the oxime were obtained[18]). $R_f(B)$ 0.23; m.p. 119–120° (dec., MeOH); $[\alpha]_D^{25} = -25.4°$ (*t* = 18 min, *c* = 1, H_2O); $[\alpha]_D^{25} = -20.4°$ (*t* = 15 h, *c* = 1, H_2O). IR (KBr): 3555*s*, 3525*s*, 3455*s*, 3380*s*, 3420*s*, 3320 (br.), 3020 (sh), 2982*m*, 2950*m*, 2925*m*, 2880*m*, 2870*m*, 1655 (sh), 1635*m*, 1459*m*, 1435*m*, 1415*s*, 1389*s*, 1365*m*, 1320*m*, 1280*m*, 1268*m*, 1232*m*, 1211*m*, 1170*m*, 1150*m*, 1131*s*, 1106*s*, 1087*s*, 1060*s*, 1046*s*, 1010*s*, 937*m*, 924*m*, 902*m*, 872*m*, 805 (br.), 765*w*, 685 (sh), 672*m*, 632*m*, 609*m*. ^{1}H-NMR (400 MHz, D_2O): 7.65 (*d*, *J* = 5.9, H–C(1)); 4.58 (*dd*, *J* = 6.9, 5.9, H–C(2)); 4.58 (*d*, *J* = 7.9, H–C(1′)); 4.01 (*dd*, *J* = 6.9, 1.8, H–C(3)); 3.98–3.88 (*m*, 4 H); 3.79–3.76 (*J* = 11.2, 6.0, 4.0, H–C(6), H–C(6′)); 3.52 (*ddd*, *J* = 9.2, 6.0, 4.0, H–C(5′)); 3.49–3.45 (*m*, 2 H); 3.37 (*dd*, *J* = 9.0, 7.9, H–C(2′)). ^{13}C-NMR (50.4 MHz, (D_6)DMSO, *t* = 13.5 min): 151.4 (*d*, C(1)); 103.8 (*d*, C(1′)); 81.0, 77.0, 76.7, 74.1, 72.0, 71.4, 70.3, 69.1 (8*d*, C(2), C(2′), C(3), C(3′), C(4), C(4′), C(5), C(5′)); 62.4, 61.4 (2*t*, C(6), C(6′)). ^{13}C-NMR (25.2 MHz, D_2O, *t* = 24 h): 150.6 (*d*, C(1)); 101.3 (*d*, C(1′)); 76.8, 74.7, 74.5, 72.3, 70.1, 68.3 (6*d*, C(2), C(2′), C(3), C(3′), C(4), C(4′), C(5), C(5′)); 61.1, 59.5 (2*t*, C(6), C(6′)). FAB-MS: 358 ($M^+ + 1$), 196. Anal. calc. for $C_{12}H_{23}NO_{11}$ (357.312): C 40.34, H 6.49, N 3.92; found: C 40.19, H 6.29, N 3.70.

4. D-*Gluconhydroximo-1,5-lactone* (**2a**). According *2.2.1*: 30 min, r.t.: yield 86%. According *2.2.2*: yield 43%. $R_f(A)$ 0.31; m.p. 190–191° (dec., MeOH); $[\alpha]_D^{25} = +88.8°$ (*c* = 1.02, H_2O). IR (KBr): 3330 (br.), 3230 (sh), 2950 (sh), 2910 (br.), 1678*s*, 1517*m*, 1505 (sh), 1450*m*, 1437*m*, 1415*m*, 1379*s*, 1340*m*, 1290*m*, 1260*w*, 1241 (sh), 1207*w*, 1139*s*, 1128*s*, 1110*m*, 1090*m*, 1073*s*, 1036*s*, 1025 (sh), 982*w*, 968*s*, 942*w*, 822*s*, 780*w*. ^{1}H-NMR (400 MHz, D_2O): 4.80 (DHO); 4.26 (*d*, *J* = 8.1, H–C(2)); 4.10 (*m*, H–C(5)); 4.06, 3.95 (*J* = 13.0, 4.5, 2.1, 2 H–C(6)); 3.80 (*dd*, *J* = 8.1, 1.1, H–C(3)); 3.79 (*dd*, *J* = 4.8, 1.1, H–C(4)). ^{13}C-NMR (50.4 MHz, D_2O): 156.5 (*s*, C(1)); 81.7 (*d*); 76.3 (*d*); 70.3 (*d*); 69.4 (*d*); 61.5 (*t*, C(6)). EI-MS: 194 (2, $M^+ + 1$), 193 (1, M^+), 176 (3), 175 (2), 164 (7), 159 (4), 158 (3), 128 (5), 115 (6), 114 (6), 104 (5), 103 (12), 102 (7), 91 (28), 86 (15), 85 (30), 74 (84), 73 (100), 72 (25), 71 (47), 69 (22), 61 (54), 60 (46), 57 (59). Anal. calc. for $C_6H_{11}NO_6$ (193.155): C 37.71, H 5.74, N 7.25; found: C 37.58, H 6.01, N 7.41.

D-*Gluconhydroximo-1,4-lactone* (**3a**). According *2.2.2*: yield 5%. According *2.2.3*: 3 h; yield 88%; $R_f(A)$ 0.34; m.p. 158–159° (dec., EtOH); $[\alpha]_D^{25} = +16.4°$ (*c* = 1.03, H_2O). IR (KBr): 3450*s*, 3360*s*, 3270*s*, 2970*m*, 2950*m*, 2940*m*, 2890 (sh), 2800*w*, 1705 (sh), 1695*s*, 1481*m*, 1450*s*, 1425*w*, 1390*m*, 1355*w*, 1333*m*, 1320*w*, 1285*s*, 1232*s*, 1220 (sh), 1190*m*, 1148*w*, 1100*m*, 1072*s*, 1060*s*, 1042*s*, 1020*s*, 990*m*, 958*s*, 950*s*, 921*m*, 880*s*, 863*m*, 801*m*, 757*m*, 648*m*. ^{1}H-NMR (200, MHz, D_2O): 4.80 (DHO); 4.65 (*dd*, *J* = 6.1, 2.8, H–C(4)); 4.48 (*d*, *J* = 1.4, H–C(2)); 4.41 (*dd*, *J* = 2.8, 1.4, H–C(3)); 4.05 (*ddd*, *J* = 8.4, 5.2, 2.4, H–C(5)); 3.92, 3.79 (*J* = 11.6, 5.2, 2.4, 2 H–C(6)). ^{13}C-NMR (50.4 MHz, D_2O): 161.0 (*s*, C(1)); 84.7 (*d*); 75.0 (*d*); 74.5 (*d*); 69.1 (*d*); 64.0 (*t*, C(6)). EI-MS: 141 (7), 115 (6), 111 (6), 103 (8), 100 (7), 97 (22), 85 (17), 74 (15), 73 (62), 72 (14), 61 (58), 57 (31), 44 (100), 43 (65), 42 (22), 39 (18).

Cellobionhydroximo-1,5-lactone (**4a**). According *2.2.1*: 17 h, r.t.; yield 35%. $R_f(B)$ 0.28; m.p. 104–106° (dec., MeOH/EtOH/MeCN); $[\alpha]_D^{25} = +35.6°$ (*c* = 1.17, H_2O). IR (KBr): 3380 (br.), 2920*m*, 2890*m*, 1672*s*, 1645 (sh), 1420 (br.), 1385*m*, 1252*m*, 1191*m*, 1167*m*, 1103*s*, 1076*s*, 1035*s*, 997*s*, 965*m*, 910*w*, 856*m*, 735 (sh), 645 (br.), 608*w*. ^{1}H-NMR (400 MHz, D_2O): 4.80 (DHO); 4.58 (*d*, *J* = 7.9, H–C(1)); 4.32 (*ddd*, *J* = 9.7, 3.9, 2.1, H–C(5′)); 4.25 (*d*,

[17]) Evaporation of the mother liquors afforded 30.7 g (13%) of the oxime as syrup.

[18]) Cellobiose oxime was obtained as syrup by *Zemplén* [40] and characterized as its octa-acetate.

J = 6.4, H–C(2)); 4.06, 3.93 (J = 12.8, 3.9, 2.1, H–C(6), H–C(6')); 4.05, 3.75 (J = 12.3, 6.1, 5.8, H–C(6), H–C(6')); 3.95 (*dd*, J = 9.8, 6.4, H–C(3)); 3.93 (*dd*, J = 9.8, 2.1, H–C(4)); 3.52 (*t*, J = 9.3, 9.3, H–C(3')); 3.50 (*m*, J = 6.1, 5.8, 2.1, H–C(5)); 3.43 (*dd*, J = 9.7, 9.3, H–C(4)); 3.34 (*dd*, J = 9.3, 7.9, H–C(2')). ^{13}C-NMR (25.2 MHz, D_2O): 154.7 (*s*, C(1)); 103.4 (*d*, C(1')); 78.5 (*d*); 78.1 (*d*); 76.2 (*d*); 75.8 (*d*); 73.6 (*d*); 73.4 (*d*); 69.8 (*d*); 68.8 (*d*); 61.0, 60.2 (2*t*; C(6), C(6')). FAB-MS: 356 ($M^+ + 1$). Anal. calc. for $C_{12}H_{21}NO_{11}$ (355.296): C 40.57, H 5.96, N 3.94; found: C 40.78, H 6.10, N 3.88.

D-*Galactonhydroximo-1,4-lactone* (**5a**). According *2.2.1*: 12 h, r.t.; yield 12%. According *2.2.2*: yield 32%. According *2.2.3*: 15 h; yield 83%. Syrup; $R_f(A)$ 0.38; $[\alpha]_D^{25} = -16.6°$ (c = 0.84, H_2O). IR (KBr): 3460–3240 (br.), 2935*m*, 2900 (sh), 1702*s*, 1634*m*, 1410*s*, 1385*m*, 1320*m*, 1250*m*, 1230*m*, 1196*m*, 1122*s*, 1098*s*, 1046*s*, 1010 (sh), 960*s*, 891*m*, 869*m*, 773*m*, 707*m*, 610 (br.). ^{1}H-NMR (400 MHz, D_2O): 4.80 (DHO); 4.72 (*m*, H–C(2)); 4.30 (*m*, H–C(3), H–C(4)); 3.93 (*ddd*, J = 7.5, 5.0, 2.5, H–C(5)); 3.78, 3.74 (J = 11.5, 7.5, 5.0, 2 H–C(6)). ^{13}C-NMR (25.2 MHz, D_2O): 158.7 (*s*, C(1)); 83.6 (*d*); 74.6 (*d*); 73.9 (*d*); 70.0 (*d*); 62.4 (*t*). FAB-MS: 238 ($M^+ - 1 + 46$), 216 ($M^+ + 23$), 194 ($M^+ + 1$).

D-*Mannonhydroximo-1,5-lactone* (**6a**). According *2.2.1*: 18 h, 40°; yield 14%. According *2.2.2*: yield 23%; $R_f(A)$ 0.28; m.p. 150–151° (dec., EtOH); $[\alpha]_D^{25} = +78.1°$ (c = 1.03, H_2O). IR (KBr): 3340 (br.), 2960*m*, 2935*m*, 2880 (br.), 1696*m*, 1680*s*, 1640 (sh), 1480*m*, 1460*m*, 1450*m*, 1410*w*, 1370 (br.), 1340 (br.), 1310*m*, 1246*s*, 1220*m*, 1208*w*, 1138*s*, 1126*s*, 1099*m*, 1050*s*, 1113*s*, 1005 (sh), 960*m*, 941*s*, 929*w*, 892*m*, 834*m*, 832*w*, 795*m*, 710*m*, 611*m*, 601*w*. ^{1}H-NMR (200 MHz, D_2O): 4.80 (DHO); 4.49 (*d*, J = 3.2, H–C(2)); 4.08–3.83 (*m*, 5 H). ^{13}C-NMR (25.2 MHz, D_2O): 156.4 (*s*, C(1)); 82.3 (*d*); 73.0 (*d*); 67.9 (*d*); 66.9 (*d*); 61.7 (*t*, C(6)). Anal. calc. for $C_6H_{11}NO_6$ (193.155): C 37.31, H 5.74, N 7.25; found: C 37.04, H 5.67, N 7.27.

2-Acetamido-2-deoxy-D-*gluconhydroximo-1,4-lactone* (**7a**). According *2.2.1*: 5 h, 40°; yield 41%. According to *2.2.2*: yield 14%; $R_f(A)$ 0.36; m.p. 194–195 (dec., MeOH); $[\alpha]_D^{25} = +44.7°$ (c = 1.08, H_2O). IR (KBr): 3380 (br.), 3290 (br.), 3140 (br.), 3100 (br.), 2930*m*, 2890*m*, 1705*s*, 1639*s*, 1564*s*, 1472*w*, 1450*w*, 1430*w*, 1379*m*, 1345*s*, 1310*w*, 1288*m*, 1240*m*, 1200*m*, 1110*s*, 1079*s*, 1051*m*, 1019*m*, 1011*m*, 994*m*, 972*s*, 960 (sh), 921*m*, 900*m*, 850*w*, 790*m*, 770 (br.), 675 (br.), 640*m*, 610*m*. ^{1}H-NMR (200 MHz, D_2O): 4.80 (DHO); 4.67 (*d*, J = 2.0, H–C(2)); 4.57 (*dd*, J = 8.0, 3.6, H–C(4)); 4.47 (*dd*, J = 3.6, 2.0, H–C(3)); 4.07 (*m*, H–C(5)); 3.92, 3.79 (J = 11.6, 5.0, 2.6, 2 H–C(6)); 2.04 (*s*, CH_3). ^{13}C-NMR (25.2 MHz, D_2O): 173.9 (*s*, CH_3CO); 158.3 (*s*, C(1)); 83.7 (*d*); 73.2 (*d*); 68.9 (*d*); 63.1 (*t*, C(6)); 56.9 (*d*, C(2)); 22.2 (*q*, CH_3). FAB-MS: 257 ($M^+ + 23$), 235 ($M^+ + 1$). Anal. calc. for $C_8H_{14}N_2O_6$ (234.208): C 41.03, H 6.03, N 11.96; found: C 40.88, H 6.06, N 12.09.

2-Acetamido-2-deoxy-D-*gluconhydroximo-1,5-lactone* (**8a**). According *2.2.1*: 5 h, 40°; yield 51%. According *2.2.2*: yield 55%. Foam; $R_f(A)$ 0.30; $[\alpha]_D^{25} = +77.8°$ (c = 1.08, H_2O). IR (KBr): 3350 (br.), 2910*m*, 2880*m*, 1655*s*, 1640*m*, 1550 (br.), 1425 (br.), 1375 (br.), 1317 (br.), 1250*m*, 1195*w*, 1215 (br.), 1050 (br.), 998*m*, 940*m*, 905*w*, 855*m*, 740*w*, 605*m*. ^{1}H-NMR (400 MHz, D_2O): 4.80 (DHO); 4.54 (*d*, J = 9.5, H–C(2)); 4.03 (J = 12.0, 1.0, H–C(6)); 3.97 (*ddd*, J = 9.0, 4.0, 1.0, H–C(5)); 3.92 (J = 12.0, 4.0, H–C(6)); 3.83 (*t*, J = 9.0, H–C(4)); 3.76 (*t*, J = 9.5, H–C(3)). ^{13}C-NMR (25.2 MHz, D_2O): 173.9 (*s*, CH_3CO); 153.1 (*s*, C(1)); 80.8 (*d*); 72.6 (*d*); 68.0 (*d*); 60.1 (*t*, C(6)); 51.1 (*d*, C(2)); 22.2 (*q*, CH_3). FAB-MS: 257 ($M^+ + 23$), 235 ($M^+ + 1$). Anal. calc. for $C_8H_{14}N_2O_5$ (234.208): C 41.03, H 6.03, N 11.96; found: C 40.65, H 6.39, N 11.72.

D-*Ribonhydroximo-1,4-lactone* (**9a**). According *2.2.2*: 23%. According *2.2.3*: 2 h, r.t.; 28%; $R_f(A)$ 0.32; m.p. 162–163° (dec., EtOH); $[\alpha]_D^{25} = +6.5°$ (c = 0.75, H_2O). IR (KBr): 3525*s*, 3470*s*, 3300 (br.), 3100 (br.), 2940*m*, 2860 (br.), 1699*s*, 1660*w*, 1635 (br.), 1475*w*, 1460*m*, 1420*w*, 1402*m*, 1370*w*, 1330*w*, 1298*m*, 1268*m*, 1252*w*, 1239*m*, 1220*m*, 1196*m*, 1158*s*, 1100 (sh), 1090*s*, 1047*s*, 1030*m*, 1005*m*, 970*s*, 921*s*, 827*m*, 788*s*, 731*m*, 665 (br.), 612*m*, 599*s*. ^{1}H-NMR (200 MHz, D_2O): 4.80 (DHO); 4.68 (*d*, J = 6.7, H–C(2)); 4.32 (*m*, J = 6.5, 4.8, 2.5, H–C(4)); 4.18 (*dd*, J = 6.7, 6.5, H–C(3)); 3.95, 3.79 (J = 13.2, 4.8, 2.5, 2 H–C(5)). ^{13}C-NMR (25.2 MHz, D_2O): 160.5 (*s*, C(1)); 88.1 (*d*); 70.5 (*d*); 69.5 (*d*); 61.1 (*t*, C(5)). Anal. calc. for $C_5H_9NO_5$ (163.129): C 36.81, H 5.56, N 8.59; found: C 37.10, H 5.71, N 8.28.

D-*Ribonhydroximo-1,5-lactone* (**10a**) was obtained as a mixture with **9a** and was characterized as the peracetate **10b**. According *2.2.1*: 1 h; R_f 0.32.

D-*Arabinonhydroximo-1,4-lactone* (**11a**). According *2.2.2*: 22%; $R_f(A)$ 0.47; m.p. 163–164° (dec., EtOH); $[\alpha]_D^{25} = -25.8°$ (c = 1.09, H_2O). IR (KBr): 3550*s*, 3360 (br.), 3260 (br.), 2960*m*, 2920*m*, 2850*m*, 2805*m*, 1691*s*, 1650*w*, 1447*m*, 1420*s*, 1401*m*, 1349*m*, 1335*s*, 1290*m*, 1259*s*, 1238*m*, 1195*m*, 1146*m*, 1130*s*, 1105*m*, 1093*m*, 1062*s*, 1049*m*, 1032*s*, 1003*s*, 959*s*, 937*s*, 848*s*, 775 (sh), 740*m*, 632*s*. ^{1}H-NMR (200 MHz, D_2O): 4.80 (DHO); 4.78 (*d*, J = 5.4, H–C(2)); 4.56 (*dd*, J = 7.4, 5.4, H–C(3)); 4.36 (*m*, H–C(4)); 3.93, 3.79 (J = 13.0, 3.6, 3.6, 2 H–C(5)). ^{13}C-NMR (25.2 MHz, D_2O): 159.8 (*s*, C(1)); 85.8 (*d*); 74.9 (*d*); 74.7 (*d*); 61.0 (*t*, C(5)). EI-MS: 164 (2, $M^+ + 1$), 163 (8, M^+), 146 (3), 145 (6), 134 (2), 128 (2), 127 (2), 116 (3), 115 (7), 114 (4), 102 (6), 98 (5), 91 (12), 90 (14), 86 (6), 85 (13), 76 (4), 75 (7), 74 (59), 73 (50), 72 (18), 71 (12), 61 (56), 60 (49), 58 (12), 57 (100), 56 (64), 55 (24), 46 (14), 45 (53), 44 (70), 43 (56), 42 (16), 33 (10), 31 (10). Anal. calc. for $C_5H_9NO_5$ (163.129): C 36.81, H 5.56, N 8.59; found: C 36.97, H 5.37, N 8.40.

D-*Arabinonhydroximo-1,5-lactone* (**12a**). Unstable compound; was characterized as the peracetate **12b**. $R_f(A)$ 0.37.

5. D-*Gluconhydroximo-1,5-lactone 1-*N,*2,3,4,6-Pentaacetate* (**2b**). Following *2.3*, **2b** was obtained in a yield of 90% as syrup (MPLC; 32 g/*C*). $R_f(C)$ 0.25; $[\alpha]_D^{25} = +78.1°$ (*c* = 1.21, $CHCl_3$). IR: 3020 (br.), 2960*w*, 2930 (sh), 1775 (sh), 1663*s*, 1658 (sh), 1655 (sh), 1647 (sh), 1635 (sh), 1460 (sh), 1450 (sh), 1435 (sh), 1428*m*, 1375 (sh), 1370*s*, 1275 (sh), 1220 (br.), 1185*s*, 1095*m*, 1065 (sh), 1042*s*, 998*m*, 955*w*, 935 (br.), 890*w*, 880 (sh). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.54 (*d*, *J* = 3.4, H–C(2)); 5.23 (*dd*, *J* = 4.2, 3.4, H–C(3)); 5.16 (*dd*, *J* = 9.8, 4.2, H–C(4)); 4.66 (*m*, *J* = 9.8, 3.4, 3.4, H–C(5)); 4.38, 4.36 (*J* = 3.4, 3.4, 2 H–C(6)); 2.19, 2.17, 2.14, 2.10, 2.10 (5*s*, 5 CH_3). ^{13}C-NMR (25.2 MHz/$CDCl_3$): 170.0, 168.7, 168.6, 167.6, 167.3 (5*s*, 5 CH_3CO); 153.5 (*s*, C(1)); 74.6 (*d*); 71.1 (*d*); 68.4 (*d*); 67.4 (*d*); 61.2 (*t*, C(6)); 20.5, 20.4, 19.2 (3*q*, 5 CH_3). EI-MS: 404 (6, $M^+ + 1$), 403 (13, M^+), 362 (20), 361 (100), 302 (20), 301 (40), 260 (13), 259 (46), 243 (26), 242 (100), 241 (23), 217 (30), 216 (13), 200 (62), 199 (100), 187 (16), 186 (31), 185 (14), 183 (70), 181 (29), 171 (22), 170 (14), 169 (30), 168 (28), 167 (22), 158 (37), 157 (100), 156 (60), 155 (85), 145 (40), 144 (48).

D-*Gluconhydroximo-1,4-lactone 1-*N,*2,3,5,6-Pentaacetate* (**3b**). Following *2.3*, **3b** was obtained in quant. yield. $R_f(C)$ 0.26; m.p. 145–146° (CH_2Cl_2/hexane); $[\alpha]_D^{25} = +32.1°$ (*c* = 1.30, $CHCl_3$). IR: 3020*m*, 2970 (sh), 1775 (sh), 1755*s*, 1686*s*, 1426 (br.), 1371*s*, 1235 (br.), 1185*s*, 1098 (sh), 1072*m*, 1042*s*, 997*m*, 967*m*, 938*s*, 894*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.55 (*d*, *J* = 3.2, H–C(3)); 5.54 (*s*, H–C(2)); 4.96 (*dd*, *J* = 9.6, 3.2, H–C(4)); 4.65, 4.23 (*J* = 12.6, 4.4, 2.6, 2 H–C(6)); 2.19, 2.16, 2.13, 2.10, 2.03 (5*s*, 5 CH_3). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.2, 169.1, 168.3, 168.0, 167.3 (5*s*, 5 CH_3CO); 159.0 (*s*, C(1)); 82.0 (*d*); 73.3 (*d*); 71.3 (*d*); 66.3 (*d*); 62.3 (*t*, C(6)); 20.7, 20.6, 20.5, 20.4, 19.2 (5*q*, 5 CH_3). EI-MS: 403 (1, M^+), 362 (1), 361 (4), 302 (1), 301 (3), 259 (2), 243 (1), 242 (1), 241 (1), 228 (1), 217 (1), 216 (1), 200 (2), 199 (3), 158 (5), 151 (23), 149 (4), 140 (3), 139 (8), 123 (17), 122 (3), 115 (4), 109 (4), 105 (4), 99 (4), 98 (5), 97 (8), 96 (19), 95 (5), 86 (8), 81 (9), 71 (12), 70 (8), 69 (13), 57 (20), 55 (14), 43 (100), 41 (15). Anal. calc. for $C_{16}H_{21}NO_{11}$ (403.340): C 47.65, H 5.25, N 3.47; found: C 47.39, H 5.00, N 3.52.

*Cellobionhydroximo-1,5-lactone 1-*N,*2,2',3,3',4',6,6'-Octaacetate* (**4b**). Following *2.3*, **4b** was obtained in a yield of 79% as crystals. $R_f(G)$ 0.40; m.p. 134–135° (CH_2Cl_2/Et_2O/hexane); $[\alpha]_D^{25} = +51.0$ (*c* = 1.24, $CHCl_3$). IR: 3030*w*, 3000*w*, 2960*w*, 2945 (sh), 2880 (sh), 1755*s*, 1665*s*, 1450 (sh), 1435 (sh), 1428*m*, 1368*s*, 1240 (br.), 1195 (sh), 1168 (sh), 1095 (sh), 1063*s*, 1042*s*, 1000*m*, 955 (sh), 932 (br.), 905*w*, 875 (sh), 830 (sh), 680*w*, 630*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.66 (*dd*, *J* = 3.4, 1.7, H–C(3)); 5.52 (*dd*, *J* = 3.4, 1.2, H–C(2)); 5.20 (*t*, *J* = 9.3, 9.3, H–C(3')); 5.07 (*t*, *J* = 9.4, 9.4, H–C(4')); 4.95 (*dd*, *J* = 9.3, 8.1, H–C(2')); 4.78 (*d*, *J* = 8.1, H–C(1')); 4.55 (*ddd*, *J* = 9.3, 5.1, 2.2, H–C(5')); 4.44, 4.18 (*J* = 12.5, 5.1, 2.2, H–C(6), H–C(6')); 4.26, 4.08 (*J* = 12.3, 4.4, 2.2, H–C(6), H–C(6')); 3.28 (*m*, *J* = 7.8, 1.7, H–C(4)); 3.78 (*m*, *J* = 7.8, 4.4, 2.2, H–C(5)). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.2, 169.9, 169.8, 169.1, 169.0, 168.7, 167.6, 167.4 (8*s*, 8 CH_3CO); 153.8 (*s*, C(1)); 101.0 (*d*, C(1')); 77.0 (*d*); 75.3 (*d*); 72.6 (*d*); 71.9 (*d*); 71.2 (*d*); 68.8 (*d*); 67.8 (*d*); 66.4 (*d*); 61.9 (*t*); 61.5 (*t*); 20.6, 20.4, 19.2 (3*q*, 8 CH_3). EI-MS: 692 (1, $M^+ + 1$), 632 (1), 601 (1), 600 (2), 599 (1), 576 (1), 548 (1), 547 (2), 533 (2), 532 (1), 531 (3), 530 (9), 529 (2), 516 (1), 515 (1), 487 (3), 475 (3), 402 (3), 390 (10), 381 (30), 258 (25), 245 (20), 200 (13), 170 (13), 169 (73), 157 (38), 156 (31), 139 (42), 115 (53), 109 (55), 103 (57), 98 (52), 97 (96), 85 (95), 81 (43), 60 (100), 56 (8), 55 (5), 54 (19). Anal. calc. for $C_{28}H_{37}NO_{19}$ (691.592): C 48.63, H 5.39, N 2.03; found: C 48.90, H 5.45, N 2.19.

D-*Galactonhydroximo-1,4-lactone 1-*N,*2,3,5,6-Pentaacetate* (**5b**). Following *2.3*, **5b** was obtained in a yield of 91% as a syrup (MPLC; 32 g/*C*). $R_f(C)$ 0.18; $[\alpha]_D^{25} = +42.8°$ (*c* = 1.21, $CHCl_3$). IR: 3015 (br.), 2960*w*, 2930 (sh), 1750*s*, 1684*s*, 1650 (sh), 1465 (sh), 1455 (sh), 1450 (sh), 1427*m*, 1370*s*, 1315 (sh), 1220 (sh), 1095 (sh), 1049*s*, 1000*s*, 937*m*, 886*w*, 860 (sh), 838*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.87 (*d*, *J* = 3.1, H–C(2)); 5.43 (*m*, *J* = 6.4, 5.2, 4.2, H–C(5)); 5.24 (*t*, *J* = 3.5, 3.1, H–C(3)); 4.67 (*t*, *J* = 4.2, 3.5, H–C(4)); 4.38, 4.26 (*J* = 12.0, 6.4, 5.2, 2 H–C(6)); 2.17, 2.16, 2.15, 2.13, 2.08 (5*s*, 5 CH_3). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.1, 169.4, 168.7, 167.3 (4*s*, 5 CH_3CO); 159.0 (*s*, C(1)); 85.0 (*d*); 75.0 (*d*); 72.8 (*d*); 68.9 (*d*); 61.8 (*t*, C(6)); 20.7, 20.6, 19.2 (3*q*, 5 CH_3). Anal. calc. for $C_{16}H_{21}NO_{11}$ (403.340): C 47.65, H 5.25, N 3.47; found: C 47.90, H 5.49, N 3.28.

D-*Mannonhydroximo-1,5-lactone 1-*N,*2,3,4,6-Pentaacetate* (**6b**). Following *2.3*, **6b** was obtained in yield of 66% as syrup (MPLC, 32 g/*D*). $R_f(D)$ 0.33; $[\alpha]_D^{25} = -9.7°$ (*c* = 1.15, $CHCl_3$). IR: 3020*s*, 2960*w*, 1755*s*, 1656*s*, 1450 (sh), 1426*m*, 1369*s*, 1306*w*, 1220 (br.), 1160 (sh), 1100*m*, 1053*s*, 1035 (sh), 1000*s*, 953*m*, 931*m*, 908*m*, 895 (sh), 825*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.99 (*d*, *J* = 3.0, H–C(2)); 5.33 (*m*, 2 H); 4.37 (*m*, 3 H); 2.18, 2.17, 2.14, 2.12, 2.08 (5*s*, 5 CH_3). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.0, 169.1, 169.0, 168.6, 167.4 (5*s*, 5 CH_3CO); 153.8 (*s*, C(1)); 77.2 (*d*); 69.2 (*d*); 66.1 (2*d*); 61.9 (*t*, C(6)); 20.5, 19.3, 19.2 (3*q*, 5 CH_3). EI-MS: 403 (1, M^+), 361 (2), 259 (1), 199 (3), 169 (1), 157 (3), 156 (1), 155 (1), 140 (2), 139 (5), 127 (3), 115 (3), 109 (3), 97 (4), 85 (3), 81 (4), 71 (12), 68 (4), 67 (2), 57 (4), 55 (5), 44 (3), 43 (100), 42 (2), 41 (6), 40 (7), 39 (2).

*2-Acetamido-2-deoxy-*D-*gluconhydroximo-1,4-lactone 1-*N,*3,5,6-Tetraacetate* (**7b**). Following *2.3*, **7b** was obtained in a yield of 93% as a syrup (MPLC; 32 g/*E*). $R_f(E)$ 0.38; $[\alpha]_D^{25} = +37.2°$ (*c* = 1.30, $CHCl_3$). IR: 3445 (*sh*),

3430*m*, 3320 (br.), 3030*w*, 2995*m*, 2950 (sh), 1750*s*, 1685 (sh), 1678 (sh), 1505 (br.), 1431 (br.), 1369*s*, 1065 (sh), 1038 (br.), 1000*s*, 940*m*, 908 (sh), 870 (sh). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.89 (*d*, *J* = 6.6, NH); 5.50 (*dd*, *J* = 4.0, 1.0, H–C(3)); 5.34 (*m*, H–C(4), H–C(5)); 4.67, 4.19 (*J* = 12.5, 4.0, 2.0, 2 H–C(6)); 4.41 (*dd*, *J* = 6.6, 1.0, H–C(2)); 2.16, 2.11, 2.07, 2.02, 1.98 (5*s*, 5 CH_3). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.4, 170.2, 169.1, 168.6, 168.1 (5*s*, 5 CH_3CO); 161.9 (*s*, C(1)); 82.5 (*d*); 74.5 (*d*); 66.9 (*d*); 62.3 (*t*, C(6)); 56.9 (*d*, C(2)); 22.1, 20.5, 20.5, 20.4, 19.0 (5*q*, 5 CH_3).

*2-Acetamido-2-deoxy-*D*-gluconhydroximo-1,5-lactone 1-*N*,3,4,6-Tetraacetate* (**8b**). Following *2.3*, **8b** was obtained in a yield of 96% as a syrup (MPLC; 32 g/*E*). $R_f(E)$ 0.28; $[\alpha]_D^{25}$ = +32.2° (*c* = 1.24, $CHCl_3$). IR: 3435*m*, 3325 (br.), 3025 (sh), 2995*m*, 2960 (sh), 2940 (sh), 2910 (sh), 1750*s*, 1685*s*, 1655 (sh), 1645 (sh), 1642*s*, 1505 (br.), 1422 (br.), 1365*s*, 1300 (sh), 1110*m*, 1065*m*, 1045*s*, 1000*s*, 950 (sh), 935 (br.), 890 (br.). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.38 (*d*, *J* = 9.0, NH); 5.47 (*t*, *J* = 9.0, H–C(4)); 5.30 (*t*, *J* = 9.0, H–C(3)); 4.67 (*dd*, *J* = 9.0, 7.8, H–C(2)); 4.56 (*ddd*, *J* = 9.0, 4.0, 2.0, H–C(5)); 4.45, 4.29 (*J* = 13.0, 4.0, 2.0, 2 H–C(6)); 2.15, 2.13, 2.06, 2.04, 1.98 (5*s*, 5 CH_3). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.5, 170.1, 169.7, 169.0, 167.9 (5*s*, 5 CH_3CO); 158.2 (*s*, C(1)); 76.6 (*d*); 71.6 (*d*); 66.8 (*d*); 61.1 (*t*, C(6)); 50.2 (*d*, C(2)); 22.6, 20.6, 20.5, 20.4, 19.3 (5*q*, 5 CH_3).

D-*Ribonhydroximo-1,4-lactone 1-*N*,2,3,5-Tetraacetate* (**9b**). Following *2.3*, **9b** was obtained in a yield of 85% as a syrup (MPLC; 32 g/*U*). $R_f(U)$ 0.20; $[\alpha]_D^{25}$ = +13.8° (*c* = 0.98, $CHCl_3$). IR: 3020 (br.), 2960*w*, 2930 (sh), 2870*w*, 1755*s*, 1686*s*, 1452*w*, 1428*w*, 1375 (sh), 1368*s*, 1220 (br.), 1120*s*, 1085 (sh), 1072*s*, 1050 (sh), 1015 (sh), 995*m*, 950*m*, 922*w*, 887*w*, 832*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.96 (*d*, *J* = 5.8, H–C(2)); 5.47 (*dd*, *J* = 5.8, 3.0, H–C(3)); 4.82 (*m*, *J* = 3.3, 3.0, 2.6, H–C(4)); 4.44, 4.29 (*J* = 13.8, 3.3, 2.6, 2 H–C(5)); 2.19, 2.15, 2.14, 2.11 (4*s*, 4 CH_3). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 169.4, 168.9, 168.5, 167.0 (4*s*, 4 CH_3CO); 158.7 (*s*, C(1)); 83.9 (*d*); 69.6 (*d*); 67.7 (*d*); 62.0 (*t*, C(5)); 20.3, 20.0, 19.9, 18.9 (4*q*, 4 CH_3). EI-MS: 331 (1, M^+), 289 (5), 229 (1), 187 (3), 170 (1), 169 (4), 157 (1), 145 (2), 144 (3), 128 (3), 127 (13), 116 (1), 115 (6), 103 (2), 102 (1), 97 (4), 86 (2), 85 (6), 73 (2), 69 (2), 68 (1), 61 (1), 60 (3), 55 (2), 45 (4), 44 (3), 43 (100), 42 (4). Anal. calc. for $C_{13}H_{17}NO_9$ (331.277): C 47.13, H 5.17; found: C 46.86, H 5.32.

D-*Ribonhydroximo-1,5-lactone 1-*N*,2,3,4-Tetraacetate* (**10b**). Following *2.3*, **10b** was obtained in a yield of 3% as a syrup (MPLC; 32 g/*U*). $R_f(U)$ 0.21; $[\alpha]_D^{25}$ = +39.4° (*c* = 3.0, $CHCl_3$). IR: 3030*m*, 3005*m*, 2970*w*, 2940*w*, 2920*w*, 1752*s*, 1653*s*, 1648 (sh), 1428*m*, 1368*s*, 1293 (sh), 1220 (br.), 1188*s*, 1152*s*, 1122*s*, 1098*s*, 1070 (sh), 1056*s*, 1019*s*, 1000*s*, 975 (br.), 952*s*, 932 (sh), 899*s*, 885 (sh), 855 (br.), 830 (br.). ^{1}H-NMR (200 MHz, $CHCl_3$): 5.77 (*d*, *J* = 2.8, H–C(2)); 5.68 (*t*, *J* = 3.0, 2.8, H–C(3)); 5.32 (*ddd*, *J* = 8.8, 5.5, 3.0, H–C(4)); 4.39, 4.26 (*J* = 11.0, 8.8, 5.5, 2 H–C(5)); 2.18, 2.16, 2.09 (3*s*, 4 CH_3). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 169.0, 168.6, 168.2, 167.0 (4*s*, 4 CH_3CO); 153.8 (*s*, C(1)); 66.7 (*d*); 66.1 (*t*); 64.9 (*d*); 64.8 (*d*); 20.5, 20.4, 20.3, 19.3 (4*q*, 4 CH_3). Anal. calc. for $C_{13}H_{17}NO_9$ (331.277): C 47.13, H 5.17, N 4.23; found: C 47.22, H 5.05, 4.15.

D-*Arabinonhydroximo-1,4-lactone 1-*N*,2,3,5-Tetraacetate* (**11b**). Following *2.3*, **11b** was obtained in a yield of 41%. $R_f(D)$ 0.18; m.p. 110–111° (CH_2Cl_2/hexane); $[\alpha]_D^{25}$ = +23.1° (*c* = 1.15, $CHCl_3$). IR: 3020 (sh), 3000*m*, 2970 (sh), 1750*s*, 1682*s*, 1445*w*, 1423*m*, 1367*s*, 1323*w*, 1220 (br.), 1180*s*, 1100 (sh), 1080 (sh), 1037*s*, 997*s*, 985 (sh), 930*m*, 885*m*, 835 (sh). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.81 (*d*, *J* = 2.8, H–C(2)); 5.23 (*t*, *J* = 3.0, 2.8, H–C(3)); 4.71 (*m*, *J* = 5.3, 4.7, 3.0, H–C(4)); 4.46, 4.32 (*J* = 12.5, 5.3, 4.7, 2 H–C(5)); 2.19, 2.17, 2.14 (3*s*, 4 CH_3). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.0, 169.3, 168.6, 167.2 (4*s*, 4 CH_3CO); 159.3 (*s*, C(1)); 85.0 (*d*); 74.6 (*d*); 72.9 (*d*); 61.8 (*t*); 20.5 (*m*, 3 CH_3); 19.1 (*q*, CH_3). EI-MS: 331 (1, M^+), 289 (5), 229 (1), 218 (1), 216 (4), 187 (2), 175 (2), 174 (1), 170 (1), 169 (4), 145 (2), 144 (2), 141 (2), 140 (25), 135 (2), 128 (3), 127 (16), 115 (3), 113 (2), 112 (10), 99 (5), 98 (6), 97 (3), 86 (11), 85 (6), 83 (3), 69 (3), 67 (2), 55 (14), 45 (2), 44 (10), 43 (100), 42 (8), 41 (8), 39 (3). Anal. calc. for $C_{13}H_{17}NO_9$ (331.277): C 47.13, H 5.17, N 4.23; found: C 47.35, H 5.40, N 4.16.

D-*Arabinonhydroximo-1,5-lactone 1-*N*,2,3,4-Tetraacetate* (**12b**). Following *2.3*, **12b** was obtained in a yield of 14% as a syrup (MPLC; 32 g/*C*). $R_f(D)$ 0.22; $[\alpha]_D^{25}$ = +57.2 (*c* = 1.06, $CHCl_3$). IR: 3020 (sh), 3000*m*, 2960 (sh), 2900*w*, 1752*s*, 1652*s*, 1450 (sh), 1420 (br.), 1367*s*, 1285*w*, 1220 (br.), 1182*s*, 1107*m*, 1086 (sh), 1075 (sh), 1066*s*, 1040*m*, 1017*w*, 999*w*, 935*m*, 900*w*, 885*w*, 870*w*, 835*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.70 (*d*, *J* = 7.3, H–C(2)); 5.52 (*m*, *J* = 3.0, 3.0, 3.0, H–C(4)); 5.44 (*dd*, *J* = 7.3, 3.0, H–C(3)); 4.41 (*J* = 3.0, 3.0, H–C(5)); 2.18, 2.16, 2.14, 2.11 (4*s*, 4 CH_3). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 169.4, 169.2, 168.9, 167.4 (4*s*, 4 CH_3CO); 155.0 (*s*, C(1)); 68.0 (*d*); 67.8 (*t*, C(5)); 65.8 (*d*); 65.7 (*d*); 20.6 (*m*, 3 CH_3); 19.3 (*q*, 1 CH_3). EI-MS: 331 (1, M^+), 290 (1), 289 (4), 229 (1), 187 (2), 170 (2), 169 (4), 157 (1), 145 (2), 144 (2), 128 (4), 127 (9), 116 (1), 115 (4), 111 (2), 103 (2), 99 (1), 97 (6), 86 (1), 85 (6), 73 (1), 71 (1), 69 (2), 68 (1), 61 (1), 60 (2), 55 (1), 49 (1), 45 (2), 44 (3), 43 (100), 42 (3), 41 (1), 39 (1). Anal. calc. for $C_{13}H_{17}NO_9$ (331.277): C 47.13, H 5.17, N 4.23; found: C 47.08, H 5.11, N 4.15.

6. *2,3,4,6-Tetra-*O*-acetyl-*D*-gluconhydroximo-1,5-lactone* (**2c**). Following *2.4*, **2c** was obtained in a yield of 53% as a syrup; FC(*C*). $R_f(C)$ 0.26; $[\alpha]_D^{25}$ = +84.1° (*c* = 1.08, $CHCl_3$). IR: 3680 (br.), 3580*m*, 3480 (br.), 3020*m*, 2960*w*, 2930 (sh), 1755*s*, 1676*m*, 1650*w*, 1600*w*, 1500 (sh), 1475 (sh), 1450*w*, 1428*w*, 1370*s*, 1345 (sh), 1225 (br.). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.71 (br., 1 H, exch. with D_2O, OH); 5.44 (*dd*, *J* = 2.2, 2.0, H–C(2)); 5.14 (*dd*,

J = 4.3, 2.2, H–C(3)); 5.08 (*dd*, J = 9.1, 4.3, H–C(4)); 4.61 (*m*, J = 9.1, 3.3, 3.3, H–C(5)); 4.37 (J = 3.3, 3.3, 2 H–C(6)); 2.15, 2.12, 2.10, 2.09 (4*s*, 4 CH_3). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.5, 169.0, 168.3 (3*s*, 4 CH_3CO); 148.1 (*s*, C(1)); 73.6 (*d*); 71.9 (*d*); 68.5 (*d*); 67.3 (*d*); 61.4 (*t*, C(6)); 20.7 (*q*, 4 CH_3). EI-MS: 361 (2, M^+), 259 (3), 242 (2), 200 (3), 199 (8), 157 (6), 156 (2), 140 (9), 139 (11), 128 (2), 127 (5), 126 (3), 115 (4), 109 (5), 103 (2), 98 (2), 97 (6), 85 (3), 81 (30), 71 (2), 69 (3), 60 (9), 55 (2), 45 (13), 44 (5), 43 (100), 42 (10), 41 (3), 39 (3).

*2,3,5,6-Tetra-*O*-acetyl-*D*-gluconhydroximo-1,4-lactone* (**3c**). Following *2.4*, **3c** was obtained in a yield of 71% as a syrup; FC(*C*). R_f(*C*) 0.27; $[\alpha]_D^{25}$ = +44.2° (c = 1.45, $CHCl_3$). IR: 3575*s*, 3470 (sh), 3360 (br.), 3030*m*, 3010*m*, 2960 (sh), 1752*s*, 1700*s*, 1437 (sh), 1429*m*, 1370*s*, 1327*w*, 1253 (sh), 1220 (br.), 1096 (sh), 1071*s*, 1039*s*, 994 (sh), 926*m*, 935*m*, 915*m*, 842*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.67 (*s*, OH); 5.45 (*m*, H–C(2), H–C(3)); 5.30 (*ddd*, J = 9.5, 4.5, 2.7, H–C(5)); 4.61 (*dd*, J = 4.5, 3.2, H–C(4)); 4.30, 4.14 (J = 12.5, 4.4, 2.6, 2 H–C(6)); 2.13, 2.10, 2.08, 2.01 (4*s*, 4 CH_3).

*2-Acetamido-3,5,6-tri-*O*-acetyl-2-deoxy-*D*-gluconhydroximo-1,4-lactone* (**7c**). Following *2.4*, **7c** was obtained in a yield of 85% as a foam; FC(*H*). R_f(*E*) 0.27; $[\alpha]_D^{25}$ = +31.8° (c = 1.19, $CHCl_3$). IR: 3660*w*, 3580*m*, 3435*m*, 3350 (br.), 3030*w*, 2995*m*, 2930*m*, 2895*w*, 2830*w*, 1750*s*, 1687 (br.), 1601 (sh), 1510 (br.), 1450*m*, 1370*s*, 1348 (sh), 1329*w*, 1320 (sh), 1232 (br.), 1131*s*, 1113*s*, 1100*s*, 1070*s*, 1034*s*, 1008 (sh), 993*w*, 962*w*, 943*m*, 920 (sh), 870 (br.). ^{1}H-NMR (200 MHz, $CDCl_3$): 8.68 (br., OH); 7.12 (*d*, J = 6.3, NH); 5.55 (*dd*, J = 4.3, 1.7, H–C(3)); 5.36 (*m*, J = 9.1, 5.0, 2.6, H–C(5)); 4.99 (*dd*, J = 9.1, 4.3, H–C(4)); 4.55 (J = 12.3, 3.6, H–C(6)); 4.52 (*dd*, J = 6.3, 1.7, H–C(2)); 4.23 (J–12.3, 5.0, H–C(6)).

*2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*D*-gluconhydroximo-1,5-lactone* (**8c**). Following *2.4*, **8c** was obtained in a yield of 71% as a foam; FC(*H*). R_f(*H*) 0.30; $[\alpha]_D^{25}$ = +36.7° (c = 1.06, $CHCl_3$). IR: 3575*m*, 3480 (sh), 3440*s*, 3270 (br.), 3220*w*, 3030 (sh), 3005*m*, 2960*m*, 2930*m*, 2875*w*, 2860*m*, 1750 (br.), 1690*s*, 1670*s*, 1602*w*, 1530 (br.), 1430 (br.), 1370*s*, 1306*m*, 1220 (br.), 1160*w*, 1108*w*, 1065*m*, 1047*s*, 1012*m*, 947*m*, 918*w*, 795*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.56 (*s*, OH); 7.51 (*d*, J = 8.6, NH); 5.42 (*t*, J = 8.6, H–C(4)); 5.10 (*m*, H–C(2), H–C(3)); 4.34 (*m*, 2 H–C(6)); 4.24 (*m*, J = 8.6, 3.8, 2.8, H–C(5)); 2.14, 2.08, 2.06, 1.92 (4*s*, 4 CH_3).

*2,3,5-Tri-*O*-acetyl-*D*-ribonhydroximo-1,4-lactone* (**9c**). Following *2.4*, **9c** was obtained in a yield of 52% as a syrup; FC(*D*). R_f(*D*) 0.34; $[\alpha]_D^{25}$ = +37.9° (c = 1.07, $CHCl_3$). IR: 3580*m*, 3350 (br.), 3020*m*, 2950*w*, 1752*s*, 1702*m*, 1451*m*, 1428*m*, 1380*s*, 1220 (br.), 1150 (sh), 1113*m*, 1092*s*, 1065*s*, 1052 (sh), 1016*m*, 987*m*, 962*m*, 931*s*, 905 (sh), 880 (sh), 830*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.06 (*s*, OH); 5.82 (*d*, J = 5.6, H–C(2)); 5.34 (*dd*, J = 5.6, 4.0, H–C(3)); 4.71 (*m*, H–C(4)); 4.43, 4.19 (J = 12.3, 4.0, 4.0, 2 H–C(5)); 2.10 (*m*, 3 CH_3).

7. O-*(2,3,4,6-Tetra-*O*-acetyl-*D*-glucopyranosylidene)amino* N-*Methylcarbamate* (**2d**). Following *2.6*, **2d** was obtained in a yield of 84% as a foam, containing 1 equiv. of H_2O. R_f(*C*) 0.21; $[\alpha]_D^{25}$ = +64.3° (c = 1.58, $CHCl_3$). IR: 3440*m*, 3020 (sh), 3000*m*, 2950 (br.), 2890 (sh), 1750*s*, 1671*m*, 1520 (br.), 1450*w*, 1420*m*, 1370*s*, 1339 (sh), 1275 (sh), 1235 (br.), 1103*s*, 1065 (sh), 1042*s*, 1012 (sh), 960*s*, 922 (sh), 875 (br.), 633 (br.). ^{1}H-NMR (200 MHz, $CDCl_3$): 6.04 (*d*, J = 4.9, exch. with D_2O, NH); 5.48 (*d*, J = 3.0, H–C(2)); 5.18 (*dd*, J = 4.1, 3.0, H–C(3)); 5.14 (*dd*, J = 9.2, 4.1, H–C(4)); 4.65 (*m*, J = 9.2, 4.0, 2.7, H–C(5)); 4.38, 4.32 (J = 12.5, 4.0, 2.7, 2 H–C(6)); 2.9 (*d*, J = 4.9, CH_3); 2.19, 2.14, 2.12, 2.10 (4*s*, 4 CH_3); 1.68 (*s*, H_2O). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.3, 168.9, 168.8, 167.8 (4*s*, 4 CH_3CO); 154.9 (*s*, C(1)); 150.7 (*s*, OCONH); 74.4, 71.5, 68.4, 67.0 (4*d*); 61.2 (*t*, C(6)); 27.5 (*q*, CH_3N); 20.5, 20.5, 20.4 (3*q*). Anal. calc. for $C_{16}H_{22}N_2O_{11}\cdot H_2O$ (436.370): C 44.04, H 5.54, N 6.42; found: C 44.35, H 5.50, N 6.27.

O-*(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*D*-glucopyranosylidene)amino* N-*Methylcarbamate* (**8d**). Following *2.6*, **8d** was obtained in a yield of 91% as a foam. R_f(*H*) 0.21. IR: 3665*w*, 3435*s*, 3305 (br.), 3220 (sh), 3020 (sh), 3005*s*, 2975*s*, 2870*m*, 1750*s*, 1685*s*, 1660 (sh), 1610 (sh), 1540 (sh), 1520 (sh), 1510*s*, 1450*m*, 1418*m*, 1370*s*, 1305*m*, 1220 (br.), 1162*w*, 1103*m*, 1060 (sh), 1050*s*, 1015 (sh), 960*s*, 900 (br.), 830 (br.), 639 (sh). ^{1}H-NMR (90 MHz, $CDCl_3$): 7.28 (*d*, J = 7.2, NH); 6.07 (*d*, J = 4.8, OCONH); 5.55 (*m*, H–C(3), H–C(4)); 4.72 (*m*, H–C(5)); 4.06 (*dd*, J = 7.2, 3.4, H–C(2)); 3.70, 3.60 (J = 3.2, 3.0, 2 H–C(6)); 2.87 (*d*, J = 4.8, CH_3NH); 2.07, 2.04, 2.00 (3*s*, 4 CH_3CO). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.4, 170.2, 169.7, 168.9 (4*s*, 4 CH_3CO); 155.6 (*s*); 154.3 (*s*); 77.0, 71.5, 67.4 (3*d*, C(3), C(4), C(5)); 61.3 (*t*, C(6)); 49.2 (*d*, C(2)); 27.6 (*q*, CH_3N); 22.8 (*q*, CH_3CON); 20.6, 20.5 (2*q*, 3 CH_3CO).

O-*(2,3,5-Tri-*O*-acetyl-*D*-ribofuranosylidene)amino* N-*Methylcarbamate* (**9d**). Following *2.6*, **9d** was obtained in a yield of 67% as a syrup. R_f(*C*) 0.29. IR: 3440*m*, 3030 (sh), 3005*m*, 2950*w*, 2930 (sh), 2890 (sh), 2850 (sh), 1750*s*, 1693*s*, 1540 (sh), 1518*m*, 1452*w*, 1419*m*, 1378 (sh), 1370*s*, 1220 (br.), 1115 (sh), 1095*s*, 1068 (br.), 1016*m*, 999*w*, 958*m*, 899*w*, 881*w*, 860 (sh), 839*w*, 625 (sh). ^{1}H-NMR (80 MHz, $CDCl_3$): 5.85 (*d*, J = 5.7, H–C(2)); 5.41 (*dd*, J = 5.7, 3.6, H–C(3)); 4.82 (*m*, H–C(4)); 4.44, 4.42 (J = 12.5, 3.0, 2.8, 2 H–C(5)); 2.89 (*d*, J = 4.9, CH_3N); 2.15, 2.11, 2.08 (3*s*, 3 CH_3C).

O-*(D-Glucopyranosylidene)amino* N-*Methylcarbamate* (**2e**). Following *2.5*, **2f** was obtained in a yield of 96% as a foam. R_f(*A*) 0.41; $[\alpha]_D^{25}$ = +49.3° (c = 1.26, H_2O). IR (KBr): 3450 (br.), 2940*m*, 2910 (sh), 1723*s*, 1657*s*, 1545

(sh), 1522*s*, 1455*m*, 1420*m*, 1362 (br.), 1240*s*, 1205 (sh), 1112*s*, 1070*s*, 1060 (sh), 1035 (sh), 985*m*, 860*m*, 915*w*, 862*m*, 770*m*. ^{1}H-NMR (200 MHz, D_2O): 4.80 (DHO); 4.35 (*d*, *J* = 8.0, H–C(2)); 4.20 (*ddd*, *J* = 9.5, 4.1, 2.0, H–C(5)); 4.03, 3.89 (*J* = 12.5, 4.1, 2.0, 2 H–C(6)); 3.86 (*t*, *J* = 8.5, 8.0, H–C(3)); 3.79 (*dd*, *J* = 9.5, 8.5, H–C(4)); 2.82 (*s*, CH_3). ^{13}C-NMR (25.2 MHz, D_2O): 158.8, 158.0 (2*s*, OCON, C(1)); 81.7, 74.6, 69.3, 68.3 (4*d*, C(2), C(3), C(4), C(5)); 60.3 (*t*, C(6)); 27.3 (*q*, CH_3). CI-MS: 251 (2, $M^+ + 1$), 195 (3), 194 (100), 190 (3), 189 (2), 179 (4), 178 (6), 176 (23), 174 (5), 160 (12), 158 (5), 142 (5), 133 (21), 131 (10), 128 (14), 119 (7), 115 (45), 89 (46), 73 (72). Anal. calc. for $C_8H_{14}N_2O_7$ (250.207): C 38.40, H 5.64, N 11.20; found: C 38.17, H 5.59, N 11.05.

O-*(2,3,4,6-Tetra*-O-*acetyl*-D-*glucopyranosylidene)amino* N-*Phenylcarbamate* (**2f**). Following *2.6*, **2e** was obtained in a yield of 90% as a syrup. $R_f(C)$ 0.30. IR: 3430*w*, 3395*m*, 3030*m*, 3005*m*, 2960*w*, 1755*s*, 1669*m*, 1655 (sh), 1602*s*, 1598*s*, 1545 (sh), 1518 (br.), 1446*s*, 1370*s*, 1322*w*, 1310*m*, 1100*m*, 1038*s*, 1019*m*, 990 (br.), 925*m*.

O-*(*D-*Glucopyranosylidene)amino* N-*Phenylcarbamate* (**2g**). Following *2.5*, **2g** was obtained in a yield of 90% as a foam. $R_f(K)$ 0.36; $[\alpha]_D^{25} = +33.6°$ (*c* = 0.56, MeOH). IR (KBr): 3410 (br.), 3320 (sh), 3080 (sh), 2970 (sh), 2925*m*, 2880 (sh), 2820 (sh), 1748*s*, 1660*s*, 1602*s*, 1530*w*, 1548 (br.), 1530*s*, 1502*s*, 1448*s*, 1387*m*, 1330 (sh), 1320*m*, 1301 (br.), 1252 (br.), 1210*s*, 1120 (br.), 1162 (br.), 1021*s*, 1000 (sh), 975*m*, 911*m*, 875*m*, 840*w*, 795*m*, 753*s*, 697*m*, 660*m*. ^{1}H-NMR (200 MHz, CD_3OD): 7.51–7.03 (*m*, 5 arom. H): 4.28 (*ddd*, *J* = 9.5, 4.8, 2.2, H–C(5)); 4.24 (*d*, *J* = 5.5, H–C(2)); 3.97, 3.83 (*J* = 12.1, 4.8, 2.2, 2 H–C(6)); 3.83 (*m*, H–C(3)); 3.68 (*dd*, *J* = 9.5, 6.1, H–C(4)). ^{13}C-NMR (25.2 MHz, CD_3OD): 160.1 (*s*, OCON); 154.7 (*s*, C(1)); 139.2, 129.8, 124.6, 120.4 (6 arom. C); 82.4, 76.8, 71.1, 70.9 (4*d*, C(2), C(3), C(4), C(5)); 61.9 (*t*, C(6)). FAB-MS: 335 ($M^+ + 23$), 313 ($M^+ + 1$). Anal. calc. for $C_{13}H_{16}N_2O_7$ (312.278): C 50.00, H 5.16, N 8.97; found: C 50.18, H 5.10, N 9.02.

O-*(2-Acetamido-2-deoxy*-D-*glucopyranosylidene)amino* N-*Methylcarbamate* (**8e**). Following *2.5*, **8e** was obtained in a yield of 86% as a syrup. $R_f(A)$ 0.16; $[\alpha]_D^{25} = +82.3°$ (*c* = 0.47, H_2O). IR (KBr): 3400 (br.), 3120 (sh), 2940*m*, 2900 (sh), 1725*s*, 1645 (br.), 1530 (br.), 1450*w*, 1420*w*, 1375*m*, 1315*m*, 1235*s*, 1195*m*, 1235*s*, 1195*m*, 1155 (sh), 1108*s*, 1065*s*, 1040 (sh), 1000*w*, 960*m*, 910 (sh), 850*m*, 760*w*, 605*w*. ^{1}H-NMR (200 MHz, D_2O): 4.80 (DHO); 4.68 (*m*, H–C(2)); 4.12 (*m*, H–C(5)); 4.20–3.94 (*m*, 4 H); 2.90 (*s*, CH_3N); 2.22 (*s*, CH_3CO_2). ^{13}C-NMR (25.2 MHz, D_2O): 175.0 (*s*, CH_3CO); 158.3 (*s*, OCON); 156.5 (*s*, C(1)); 82.8, 72.7, 68.3 (3*d*, C(3), C(4), C(5)); 60.6 (*t*, C(6)); 51.8 (*d*, C(2)); 27.7 (*q*, CH_3N); 22.8 (*q*, CH_3CO). FAB-MS: 314 ($M^+ + 23$), 292 ($M^+ + 1$). Anal. calc. for $C_{10}H_{17}N_3O_7$ (291.60): C 41.24, H 5.88, N 14.43; found: C 40.97, H 5.99, N 14.70.

O-*(*D-*Ribofuranosylidene)amino* N-*Methylcarbamate* (**9e**). Following *2.5*, **9e** was obtained in a yield of 91% as a syrup. $R_f(A)$ 0.45; $[\alpha]_D^{25} = -23.5°$ (*c* = 1.25, H_2O). IR (KBr): 3450 (br.), 2945*m*, 2895 (sh), 1728*s*, 1681*s*, 1631 (br.), 1528*s*, 1451*m*, 1421*m*, 1383 (sh), 1368 (sh), 1353*m*, 1260*s*, 1232*s*, 1140*s*, 1110 (sh), 1080*s*, 995 (sh), 957*m*, 825*w*, 802*m*, 767*s*. ^{1}H-NMR (200 MHz, D_2O): 4.92 (*d*, *J* = 5.2, H–C(2)); 4.80 (DHO); 4.63 (*m*, *J* = 4.0, 3.2, 3.0, H–C(4)); 4.36 (*dd*, *J* = 5.2, 3.1, H–C(3)); 3.88 (*J* = 13.2, 3.0, H–C(5)); 3.74 (*J* = 13.2, 4.0, H–C(5)); 2.77 (*s*, CH_3). ^{13}C-NMR (50.4 MHz, D_2O): 163.8 (*s*); 90.4 (*d*); 70.4 (*d*); 70.1 (*d*); 60.9 (*d*); 27.5 (*t*, C(5)); 27.48 (*q*, CH_3). FAB-MS: 244 ($M^+ + 1 + 23$), 221 ($M^+ + 1$). Anal. calc. for $C_7H_{12}N_2O_6$ (220.181): C 38.19, H 5.49, N 12.72; found: C 38.44, H 5.30, N 12.49.

8. *(*E*)-2,3:5,6-Di*-O-*isopropylidene*-D-*mannonhydroximo-1,4-lactone* (**15**). Activated MnO_2 (1.26 g) was added to a stirred soln. of **13** (2.0 g, 7.3 mmol) in MeOH (20 ml). After 1.5 h, the starting material had disappeared; two new products ($R_f(C)$: 0.29 and 0.20) had been formed. The mixture was filtered through *Celite*, the filtrate evaporated *i.v.*, and the residue treated with AcOEt/hexane 1:1 (30 ml). A product (1.12 g, 56%) with R_f 0.20 (identical with **14**; see [2]) crystallized and was filtered off. MPLC (100 g/*F*) of the mother liquor afforded **15** (230 mg, 12%) and **14** (620 mg, 31%). Isomer **15** was recrystallized from CH_2Cl_2/hexane, m.p. 125° (upon slow heating, **15** was transformed into **14**, m.p. 176°). $[\alpha]_D^{25} = +190.7°$ (*c* = 1.01, $CHCl_3$). IR: 3585*s*, 3350 (br.), 3035*w*, 2995*s*, 2940*m*, 2895*m*, 1690*s*, 1500 (sh), 1482*w*, 1452*m*, 1440 (sh), 1385*s*, 1375*s*, 1327 (br.), 1250 (br.), 1156*m*, 1121*m*, 1070*s*, 1050 (sh), 1030*m*, 1002*w*, 973*s*, 937*w*, 890*w*, 860 (sh), 840*m*, 815 (sh), 680(br.). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.14 (br., OH); 5.49 (*d*, *J* = 5.8, H–C(2)); 4.88 (*m*, H–C(3)); 4.52 (*m*, *J* = 8.0, 4.8, 4.8, H–C(5)); 4.30 (*dd*, *J* = 8.2, 3.5, H–C(4)); 4.20, 4.17 (*m*, 2 H–C(6)); 1.50, 1.47, 1.42, 1.40 (4*s*, 4 CH_3). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 164.5 (*s*, C(1)); 113.3, 109.1 (2*s*, 2 $(CH_3)_2C$); 81.1, 77.0, 75.6, 72.3 (4*d*); 66.0 (*t*, C(6)); 26.4, 26.0, 25.0, 24.7 (4*q*, 4 CH_3). EI-MS: 259 (3, $M^+ + 1 - 15$), 258 ($M^+ - 15$), 242 (1), 201 (1), 200 (7), 173 (2), 159 (2), 158 (17), 160 (4), 115 (3), 112 (5), 102 (2), 101 (41), 98 (7), 94 (5), 85 (60), 84 (4), 83 (5), 73 (12), 72 (10), 71 (7), 69 (6), 49 (38), 57 (7), 55 (7), 43 (100), 41 (18), 39 (8). Anal. calc. for $C_{12}H_{19}NO_6$ (273.285): C 52.74, H 7.01, N 5.13; found: C 52.46, H 6.76, N 5.41.

9. *2,3:5,6-Di*-O-*isopropylidene-1-nitroso*-D-*mannofuranosyl Bromide* (**16**). Following *2.7*, 310 mg (88%) of **16** were obtained. $R_f(C)$ 0.67. IR (crude): 2982*s*, 2935*m*, 2885*w*, 1726*s*, 1562*s*, 1450*m*, 1329*m*, 1321*s*, 1302*w*, 1250 (br.), 1230*w*, 1170 (sh), 1148*s*, 1135 (sh), 1110 (sh), 1085 (sh), 1067*s*, 1040 (sh), 998*m*, 968*m*, 955 (sh), 910 (sh), 886*s*, 837*s*. ^{1}H-NMR (200 MHz, $CDCl_3$; crude): 5.92 (*d*, *J* = 5.7, H–C(2)); 5.02 (*dd*, *J* = 5.7, 3.7, H–C(3)); 4.50 (*ddd*, *J* = 8.1, 5.1, 4.0, H–C(5)); 4.19 (*dd*, *J* = 8.1, 3.7, H–C(4)); 4.14, 4.01 (*J* = 9.0, 5.9, 4.0, 2 H–C(6)); 2.96 (*s*, NBS); 1.48, 1.39, 1.30, 1.24 (4*s*, 4 CH_3).

*2,3,4,6-Tetra-*O*-benzyl-1-nitroso-*D*-glucopyranosyl Bromide* (**17**). Following *2.7*, **17** was obtained in a yield of 77%. $R_f(S)$ 0.66. UV: 658 (17), 620 (sh, 12), 273 (sh, 1300), 267 (sh, 1900), 260 (sh, 2300), 257 (2400), 252 (2400), 228 (3000). CD: 658 (+2.06), 305 (−0.12). IR (crude): 3095*w*, 3065*w*, 3030 (sh), 3005*m*, 2920 (br.), 2870*m*, 1728*s*, 1690 (br.), 1566*m*, 1561 (sh), 1495*m*, 1452*s*, 1398 (br.), 1360*m*, 1345 (sh), 1308*w*, 1155*s*, 1123*m*, 1090 (br.), 1028*m*, 995 (br.), 910*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.36–7.11 (*m*, 20 arom. H); 5.01–4.46 (*m*, 8H); 4.20 (*t*, *J* = 9.0, 1 H); 4.06 (*ddd*, *J* = 9.7, 2.9, 1.5, H–C(5)); 3.87, 3.73 (*J* = 9.0, 2 H), 3.84, 3.69 (*J* = 11.6, 2.9, 1.5, 2 H–C(6)).

*2,3,5,6-Tetra-*O*-acetyl-1-nitroso-*D*-glucofuranosyl Bromide* (**18**). Following *2.7*, 332 mg (76%) of **18** were obtained as syrup. $R_f(C)$ 0.48. UV: 643 (21), 602 (13), 273 (sh, 1200), 267 (1400), 261 (1500), 228 (2750). CD: 639 (−2.44), 596 (−1.30), 283 (−0.12). ^{1}H-NMR (200 MHz, $CDCl_3$): 6.46 (*d*, *J* = 0.6, H–C(2)); 5.48 (*dd*, *J* = 4.1, 0.8, H–C(3)); 5.41 (*ddd*, *J* = 9.1, 4.9, 2.3, H–C(5)); 4.63, 4.13 (*J* = 12.7, 4.9, 2.3, 2 H–C(6)); 2.18, 2.11, 2.02, 1.97 (4*s*, 4 CH_3).

*2-Acetamido-3,5,6-tri-*O*-acetyl-2-deoxy-1-nitroso-*D*-glucofuranosyl Bromide* (**19**). Following *2.7*, **19** was obtained in a yield of 71%. $R_f(E)$ 0.62. UV: 686 (30), 637 (sh, 15), 320 (sh, 280), 253 (sh, 1100), 229 (2100). CD: 698 (+0.69), 646 (+0.23), 325 (−0.06), 316 (−0.05). IR (crude): 1569*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.51 (*d*, *J* = 3.3, H–C(3)); 5.46 (*ddd*, *J* = 9.0, 5.0, 2.4, H–C(5)); 4.70, 4.22 (*J* = 12.5, 5.0, 4.2, 2 H–C(6)); 4.47 (*dd*, *J* = 9.0, 3.3, H–C(4)); 3.99 (*d*, *J* = 1.7, H–C(2)); 2.15, 2.09, 2.05, 2.01 (4*s*, 4 CH_3).

10. *2,3,5,6-Tetra-*O*-acetyl-1-nitro-*D*-glucofuranosyl Bromide* (**24**). Following *2.9*, 324 mg (71%) of **24** was obtained. MPLC (32 g/*Q*). $R_f(Q)$ 0.19; $[\alpha]_D^{25} = -55.5°$ (*c* = 1.39, $CHCl_3$). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.98 (*d*, *J* = 1.2, H–C(2)); 5.46 (*dd*, *J* = 3.9, 1.2, H–C(3)); 5.40 (*ddd*, *J* = 8.9, 4.9, 2.6, H–C(5)); 4.94 (*dd*, *J* = 8.9, 3.9, H–C(4)); 4.61, 4.23 (*J* = 12.8, 4.9, 2.6, 2 H–C(6)); 2.17, 2.13, 2.09, 2.04 (4*s*, 4 CH_3).

*2-Acetamido-3,5,6-tri-*O*-acetyl-2-deoxy-1-nitro-*D*-glucofuranosyl Bromide* (**25**). Following *2.9*, 260 mg (57%) of **25** was obtained. M.p. 76–78° (dec., CH_2Cl_2/Et_2O/hexane); $R_f(O)$ 0.28; $[\alpha]_D^{25} = +32.8°$ (*c* = 1.03, $CHCl_3$). IR: 3020 (sh), 3000*m*, 2960 (sh), 2930*w*, 1750*s*, 1681*s*, 1580*s*, 1455 (sh), 1430*m*, 1382 (sh), 1371*s*, 1351*m*, 1220 (br.), 1160*w*, 1107*s*, 1078*m*, 1038*s*, 1013*m*, 982*s*, 962*w*, 930 (sh), 921*m*, 886*m*, 818*m*.

On standing over night at r.t., the crystals became liquid and the flask filled with red-brown vapours; a new but labile compound ($R_f(O)$ 0.22) had been formed, which on chromatography transformed into **26** (see *11*).

11. *2-Acetamido-5,6-di-*O*-acetyl-2,3-dideoxy-*D*-gluc-2-enono-1,4-lactone* (**26**). **26** *from* **40**. A soln. of **40** (50 mg, 0.3 mmol) in pyridine (3 ml) was treated in the cold with Ac_2O (1 ml). After 1 h the mixture was evaporated under high vacuum and worked up normally (CH_2Cl_2/1M $NaHCO_3$). Flash filtration (2 g, *M*) of the residue afforded **26** (56 mg, 86%) as syrup.

26 *from* **7c**. A soln. of **7c** (36 mg, 0.1 mmol) in DMSO (1 ml) containing TsOH (19 mg, 1 equiv.) was heated to 80° for 5 min. The cooled mixture was worked up normally (CH_2Cl_2/1M $NaHCO_3$). FC (2 g/*M*) of the residue afforded **26** (20 mg, 71%).

26 *from* **7c**. To a soln. of PCl_5 (42 mg, 2 mmol) in CH_2Cl_2 (5 ml) was added dropwise a soln. of **7c** (36 mg, 0.1 mmol) in CH_2Cl_2 (2 ml). When the starting material had disappeared, ice was added and the mixture stirred for 30 min. Normal workup (CH_2Cl_2/1M $NaHCO_3$) followed by FC (2 g/*M*) afforded **26** (11 mg, 39%). $R_f(M)$ 0.27. UV (EtOH): 292 (500), 245 (8500), 203 (10200). IR: 3500 (sh), 3405*s*, 3340*m*, 3130*m*, 3030*m*, 3000*m*, 1770*s*, 1750*s*, 1710*s*, 1660*s*, 1519*s*, 1435 (br.), 1370*s*, 1340*m*, 1320*s*, 1300*m*, 1235 (br.), 1121*s*, 1062*s*, 1050 (sh), 1007*m*, 958*m*, 938*m*, 851*m*, 835*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.78 (*s*, NH); 7.45 (*d*, *J* = 1.8, H–C(2)); 5.27 (*dd*, *J* = 5.6, 1.8, H–C(4)); 5.19 (*ddd*, *J* = 5.6, 5.0, 3.9, H–C(5)); 4.44, 4.16 (*J* = 12.0, 5.0, 3.9, 2 H–C(6)); 2.21 (*s*, CH_3); 2.11, 2.09 (2*s*, 2 CH_3). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 170.2, 169.5, 169.1, 168.7 (4*s*, 3 CH_3C, OCON); 126.6 (*s*, C(3)); 124.9 (*d*, C(2)); 79.1 (*d*, C(4)); 70.7 (*d*, C(5)); 61.4 (*t*, C(6)); 23.6 (*q*, CH_3); 20.7, 20.6 (2*q*, CH_3). CI-MS: 286 (100, $M^+ + 1$), 226 (65), 176 (14). Anal. calc. for $C_{12}H_{15}NO_7$ (285.189): C 50.53, H 5.30, N 4.91; found: C 50.57, H 5.37, N 5.10.

12. *(E)- and (Z)-*O*-(2,3:5,6-Di-*O*-isopropylidene-*D*-mannofuranosylidene)amino Diethyl Phosphate* (**27** and **28**, resp.). Following *2.8*, 17 mg (42%) of a 12:88 mixture **27**/**28** was obtained as syrup from **16**.

Data of **27**. $R_f(I)$: 0.21. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.26 (*d*, *J* = 5.4, H–C(2)); 4.90 (*m*, H–C(3)); 4.50 (*m*, H–C(5)); 4.42–4.04 (*m*, H–C(4), 2 H–C(6), 2 CH_3CH_2); 1.54–1.30 (*m*, $(CH_3)_2C$, 2 CH_3CH_2). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 172.4 (*d*, *J*(C,P) = 17.6, C(1)); 114.2 (*s*, $(CH_3)_2C$); 109.9 (*s*, $(CH_3)_2C$); 83.5, 78.0, 77.1, (3*d*); 72.5 (*d*); 66.4 (*t*); 64.6 (*m*, 2 CH_3CH_2); 26.9–25.1 (*m*); 16.1 (*m*, 2 CH_3CH_2).

Data of **28**. $R_f(I)$ 0.21; $[\alpha]_D^{25} = +68.5°$ (*c* = 1.25, $CHCl_3$). IR: 3030*w*, 2995*s*, 2940*m*, 2910*w*, 1677*s*, 1480*w*, 1452*m*, 1443*w*, 1384*s*, 1375*s*, 1265*s*, 1220 (br.), 1157*s*, 1121*s*, 1090 (sh), 1069*s*, 1030*s*, 971*s*, 960*s*, 932*s*, 906*m*, 850 (sh), 840*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.26 (*d*, *J* = 5.7, H–C(2)); 4.91 (*dd*, *J* = 5.7, 3.4, H–C(3)); 4.39 (*dd*,

J = 8.1, 3.4, H–C(4)); 4.34–4.19 (*m*, 2 CH_3CH_2); 4.20, 4.14 (J = 9.2, 5.0, 4.0, 2 H–C(6)); 1.49, 1.46, 1.42 (3*s*, 9 H); 1.40–1.34 (*m*, 9 H). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 162.6 (*d*, J(C,P) = 11.4, C(1)); 114.3, 109.5 (2*s*, 2 CH_3C); 83.3 (*d*); 77.8 (*d*); 77.3 (*d*); 72.4 (*d*); 66.1 (*t*, C(6)); 64.4 (*m*, 2 CH_3CH_2); 26.7, 26.6, 25.7, 25.0 (4*q*, 2 $(CH_3)_2C$); 16.1, 15.8 (2*m*, 2 CH_3CH_2). CI-MS: 410 (25, M^+ + 1), 409 (100, M^+), 394 (2), 259 (8), 256 (3), 165 (10). Anal. calc. for $C_{16}H_{28}NO_9$ (409.372): C 46.94, H 6.89, N 3.42; found: C 46.74, H 6.84, N 3.62.

28 *by Phosphorylation of* **14**. To a stirred suspension of **14** (27.3 mg, 0.1 mmol) and Bu_4NHSO_4 (0.3 mg; 1 mol-%) in CH_2Cl_2 (2 ml) and aq. NaOH (0.1M; 2.3 ml) was added diethyl phosphochloridate (22 µl; 1.5 equiv.). After 15 min the mixture was worked up as usual (CH_2Cl_2). Purification by FC (2g/*I*) afforded 34 mg (84%) of **28** as syrup.

27/**28** *by Phosphorylation of* **15**. By an analogous procedure, starting with **15**, 36 mg (89%) of a 44:56 mixture **27**/**28** was obtained as syrup.

*(*E*)- and (*Z*)-*O*-(2-Acetamido-3,5,6-tri-*O*-acetyl-2-deoxy-*D*-glucofuranosylidene)amino Diethyl Phosphate* (**29** and **30**, resp.). Following *2.8*, 189 mg of a 24:76 mixture **29**/**30** was obtained as a foam from **19**.

Data of **29**. $R_f(L)$ 0.17. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.88 (*d*, J = 7.0, NH); 5.46 (*d*, J = 3.9, H–C(3)); 5.33 (*ddd*, J = 9.3, 4.5, 2.2, H–C(5)); 5.24 (*dd*, J = 9.3, 3.9, H–C(4)); 4.74 (*d*, J = 7.0, H–C(2)); 4.60 (J = 12.0, 2.2, H–C(6)); 4.31, 4.06 (*m*, H–C(6), 2 CH_3CH_2); 2.09, 2.01 (2*s*, 2 CH_3); 1.36 (*m*, 2 CH_3CH_2). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 172.8 (*d*, J(C,P) = 18, C(1)); 170.6, 169.6, 169.1 (3*s*); 82.0 (*d*); 74.4 (*d*); 67.2 (*d*); 65.2 (*m*, 2 CH_3CH_2); 62.7 (*t*, C(6)); 56.2 (*d*, C(2)); 22.3 (*q*, CH_3CON); 20.7 (*q*); 16.1 (*m*, 2 CH_3CH_2).

Data of **30**. $R_f(L)$ 0.15. IR: 3660*w*, 3450*w*, 3430*w*, 3270 (br.), 3210*w*, 3026*w*, 2995*s*, 2930*w*, 2905*w*, 2865*w*, 1750*s*, 1682 (sh), 1679*s*, 1550 (br.), 1487*w*, 1440*m*, 1387 (sh), 1370*s*, 1285 (sh), 1252 (sh), 1220 (br.), 1162*m*, 115 (sh), 1095*m*, 1060 (sh), 1035*s*, 983*m*, 962 (sh), 951 (sh), 942*m*, 900 (sh), 862 (br.), 835*w*, 708 (br.), 658*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.68 (*d*, J = 7.5, NH); 5.51 (*dd*, J = 3.9, 1.1, H–C(3)); 5.33 (*ddd*, J = 9.3, 4.5, 2.2, H–C(5)); 5.24 (*dd*, J = 9.3, 3.9, H–C(4)); 4.61 (J = 12.6, 2.2, H–C(6)); 4.59 (*dd*, J = 7.5, 1.1, H–C(2)); 4.30–4.09 (*m*, H–C(6), 2 CH_3CH_2); 2.09, 2.07, 2.01, 2.00 (4*s*, 4 CH_3C); 1.36 (*m*, 2 CH_3CH_2). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.3, 170.2, 169.2, 168.7 (4*s*, 4 CH_3C); 162.7 (*d*, J(C,P) = 11.5, C(1)); 82.3 (*d*); 74.2 (*d*); 66.8 (*d*); 65.1, 64.8 (2*t*, 2 CH_3CH_2); 62.5 (*t*, C(6)); 56.0 (*d*, C(2)); 22.3 (*q*, CH_3CON); 20.6 (*q*, 3 CH_3CO_2); 16.1, 15.9 (2*q*, 2 CH_3CH_2). Anal. calc. for $C_{18}H_{29}N_2O_{12}P$ (496.404): C 43.55, H 5.89, N 5.64; found: C 42.29, H 6.05, N 5.49.

*(*E*)- and (*Z*)-*O*-(2,3,4,6-Tetra-*O*-benzyl-*D*-glucopyranosylidene)amino Diethyl Phosphate* (**31** and **32**, resp.). Following *2.8*, 538 mg (78%) of a 1:9 mixture **31**/**32** were obtained as syrup.

Data of **31**. $R_f(S)$ 0.32. ^{13}C-NMR (100.6 MHz, $CDCl_3$): 169.3 (C(1)); 138.1, 137.6, 137.0, 136.8 (4*s*); 128.1 (*m*); 81.0 (*d*); 78.2–76.2 (*m*); 74.2–73.5 (*m*); 73.0 (*t*); 71.5 (*t*); 70.9 (*t*); 68.4 (*t*); 67.9 (*t*); 61.8 (*m*).

Data of **32**. $R_f(S)$ 0.27; $[\alpha]_D^{25}$ = +34.2° (c = 2.81, $CHCl_3$). IR: 3090*w*, 3065*m*, 3030 (sh), 3000*s*, 2935*w*, 2910*w*, 2870*m*, 1652 (br.), 1602*w*, 1495*m*, 1452*m*, 1390*w*, 1367 (sh), 1362*m*, 1290 (sh), 1269 (br.), 1220 (br.), 1163*w*, 1110 (sh), 1095 (sh), 1070*s*, 1035 (sh), 1030*s*, 986*m*, 918 (br.), 868*w*, 692*m*, 670 (br.). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.37–7.12 (*m*, 20 arom. H); 4.67–4.58 (*m*, H–C(2), H–C(5)); 4.58, 4.57, 4.53, 4.52 (4 benzyl. H); 4.21 (*m*, 2 CH_3CH_2); 3.93 (*dd*, J = 4.0, 2.0, 1 H); 3.89–3.72 (*m*, 3 H); 1.32 (*m*, 2 CH_3CH_2). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 157.3 (*d*, J(C,P) = 11.1, C(1)); 138.1 (*s*); 137.6 (*s*); 137 (*s*); 136.7 (*s*); 128.4–127.7 (*m*); 80.7 (*d*); 77.2 (*d*); 76.9 (*d*); 73.4 (*t*); 72.9 (*t*); 72.6 (*d*); 71.5 (*t*); 70.8 (*t*); 67.8 (*t*, C(6)); 64.6, 64.3 (2*t*, 2 CH_3CH_2); 16.2, 16.0 (2*q*, 2 CH_3CH_2). CI-MS: 690 (8, M^+ + 1), 626 (8), 536 (100), 480 (42), 314 (91). Anal. calc. for $C_{38}H_{44}NO_9P$ (689.742): C 66.17, H 6.43, N 2.03; found: C 66.05, H 6.22, N 1.96.

*(*Z*)-*O*-(2,3,5,6-Tetra-*O*-acetyl-*D*-glucofuranosylidene)amino Diethyl Phosphate* (**33**). Following *2.8*, 239 mg (48%) of **33** was obtained as syrup. $R_f(O)$ 0.25; $[\alpha]_D^{25}$ = +38.4° (c = 1.75, $CHCl_3$). IR: 3025 (sh), 2995*m*, 2980 (sh), 2930*w*, 2910*w*, 2865*w*, 1755*s*, 1688*m*, 1683*m*, 1490 (sh), 1475*w*, 1458*w*, 1441*m*, 1430 (sh), 1390 (sh), 1369*s*, 1290 (sh), 1260 (sh), 1232*s*, 1220 (br.), 1161*m*, 1098*m*, 1060 (sh), 1030*s*, 980 (sh), 962*m*, 930*s*, 868*w*, 863*m*, 840 (sh), 625*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.53 (*m*, H–C(2), H–C(3)); 5.31 (*ddd*, J = 9.5, 4.1, 2.7, H–C(5)); 4.93 (*dd*, J = 9.5, 3.4, H–C(4)); 4.68 (J = 12.6, 2.7, H–C(6)); 4.34–4.12 (*m*, H–C(6), 2 CH_3CH_2); 2.16, 2.11, 2.10, 2.02 (4*s*, 4 CH_3); 1.37 (*m*, 2 CH_3CH_2). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.2, 169.1, 168.4, 167.9 (4*s*, 4 CH_3CO); 159.9 (*d*, J(C,P) = 12.2, C(1)); 81.9, 72.9, 71.5, 66.3 (4*d*, C(2), C(3), C(4), C(5)); 65.4, 64.8 (2*t*, 2 CH_3CH_2); 62.2 (*t*, C(6)); 20.5 (*q*, 4 CH_3); 16.5, 15.9 (2*q*, 2 CH_3CH_2).

13. *(1*S*)-*methylidene*,3-Anhydro-1-C-[chloro(hydroxy)methylidene]amino-1,2:4,5-di-O-isopropylidene-D-arabinitol* (**34**). A stirred soln. of **14** (219 mg, 0.8 mmol) in CH_2Cl_2 (5 ml) under N_2 was cooled in ice and treated with BuLi (1.6 M; 0.5 ml, 1 equiv.) and then with PCl_5 (200 mg, 1.2 equiv.). After stirring for 25 min, NaOH (1M, 15 ml) was added. Intense stirring was continued at r.t. until the aq. phase became clear (1 h). The org. layer was separated and washed once with NaOH (1M, 20 ml) and brine. $R_f(C)$ 0.54. IR (CH_2Cl_2, 3%): 1663*s*.

14. *(1S)-1-*C*-Aminodeoxy-1,2:4,5-di-*O*-isopropylidene-3-*D*-arabinitol-1-*N*,3-carbolactone* (**35**). A soln. of **34** (*ca.* 0.8 mmol) in CH_2Cl_2 (20 ml) was shaken 40 min with aq. HCOOH soln. (0.5M, 50 ml), the org. layer was separated, washed twice with brine, and dried (Na_2SO_4). Filtration, evaporation *i.v.*, and FC (20 g, *C*) afforded **35** (92 mg, 42%) as colourless crystals. M.p. 146.5–147.5° (CH_2Cl_2/Et_2O/hexane); R_f(*C*) 0.20; $[\alpha]_D^{25}$ = +90.0° (*c* = 0.92, $CHCl_3$). IR: 3421*s*, 3260 (br.), 3150 (br.), 3030 (sh), 2995*s*, 2940*m*, 2895*w*, 1735*s*, 1475 (sh), 1450*s*, 1405*m*, 1382*s*, 1373*s*, 1351*m*, 1322*m*, 1270*s*, 1235 (br.), 1220 (br.), 1165 (sh), 1141*s*, 1105 (sh), 1086*s*, 1070 (sh), 1036 (br.), 995 (sh), 974*m*, 960*w*, 935 (br.), 890 (sh), 873*m*, 839*m*, 630 (br.). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.79 (br., NH); 5.40 (*dd*, *J* = 6.5, 1.7, H–C(2)); 4.61 (*dd*, *J* = 6.5, 1.2, H–C(3)); 4.40 (*m*, *J* = 9.0, 5.0, 4.5, H–C(5)); 4.17, 4.16 (*J* = 9.8, 5.0, 4.5, 2 H–C(6)); 4.03 (*dd*, *J* = 9.0, 1.2, H–C(4)); 1.49, 1.44, 1.41, 1.38 (4*s*, 4 CH_3). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 152.9 (*s*, OCON); 111.6, 109.8 (2*s*, 2 $(CH_3)_2C$); 81.2 (*d*); 75.7 (*d*); 72.7 (*d*); 70.5 (*d*); 66.6 (*t*, C(6)); 27.5, 27.0, 26.5, 24.1 (4*q*, 4 CH_3). EI-MS: 259 (4), 258 (31, $M^+ - 15$), 201 (5), 200 (41), 158 (7), 157 (81), 140 (2), 115 (10), 114 (21), 102 (3), 101 (44), 100 (2), 97 (4), 96 (4), 95 (6), 86 (4), 85 (14), 84 (6), 83 (4), 73 (7), 72 (7), 71 (3), 70 (3), 69 (8), 68 (7), 59 (23), 43 (100), 41 (15), 40 (10). Anal. calc. for $C_{12}H_{19}NO_6$ (273.285): C 52.74, H 7.01, N 5.13; found: C 52.84, H 6.89, N 5.31.

15. *(1S)-*methylidene*,3-Anhydro-1-*C*-[methoxy(hydroxy)methylidene]amino-1,2:4,5-di-*O*-isopropylidene-*D*-arabinitol* (**36**). A soln. of **34** (0.8 mmol) in CH_2Cl_2 was treated with NaOMe (1M in MeOH; 1.6 ml). After 15 min, ice was added and the mixture was worked up as usual (CH_2Cl_2). Bulb-to-bulb distillation (80°/10^{-2} mbar) afforded **36** as colourless oil: 184 mg (64%). R_f(*F*) 0.30; $[\alpha]_D^{25}$ = +66.3° (*c* = 1.46, $CHCl_3$). IR: 3020 (sh), 2990*s*, 2950*s*, 2335*m*, 2910 (sh), 2890 (sh), 1675*s*, 1475 (sh), 1460 (sh), 1442*s*, 1382*s*, 1371*s*, 1341*s*, 1314*s*, 1268*s*, 1220 (br.), 1146*s*, 1070*s*, 1041*s*, 1018*m*, 971*m*, 952*w*, 941*w*, 876*m*, 840*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.43 (*d*, *J* = 4.1, H–C(2)); 4.41 (*ddd*, *J* = 8.1, 5.5, 5.0, H–C(5)); 4.33 (*dd*, *J* = 4.1, 1.6, H–C(3)); 4.16, 4.09 (*J* = 8.1, 5.5, 5.0, 2 H–C(6)); 4.12 (*dd*, *J* = 8.1, 1.6, H–C(4)); 3.77 (*s*, CH_3O); 1.45, 1.41, 1.39 (3*s*, 4 CH_3C). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 152.8 (*s*, C(1)); 111.0, 109.7 (2*s*, 2 $(CH_3)_2C$); 83.3 (*d*); 75.4 (*d*); 73.6 (*d*); 69.8 (*d*); 66.4 (*t*); 55.0 (*q*, CH_3O); 28.1, 26.9, 26.8, 25.2 (4*q*, 4 CH_3C). CI-MS: 288 (100, $M^+ + 1$), 230 (53). Anal. calc. for $C_{13}H_{21}NO_6$ (287.312): C 54.35, H 7.37, N 4.88; found: C 54.35, H 7.36, N 5.01.

16. *(1R)- and (1S)-1-*C*-Amino-1,2,3,5-tetra-*O*-benzyl-4-deoxy-*D*-arabinitol-1-*N*,4-carbolactone* (**37** and **38**, resp.) *and 2,3,5-Tri-*O*-benzyl-4-*O*-carbamoyl-*D*-arabinose* (**39**). To an ice cold stirred soln. of **1** (488 mg, 0.88 mmol) in CH_2Cl_2 (25 ml) was added PCl_5 (219 mg, 1.2 equiv.). After 1 h, H_2O (2 ml) was added and the ice-bath removed. After 1 h, the mixture was poured into 1M K_2CO_3 soln. (100 ml) and shaken until the aq. phase became clear. Normal workup (CH_2Cl_2) gave 450 mg of a slightly yellow syrup, which quickly turned red-brown. FC (50 g/*N*) afforded 2 fractions: R_f 0.26: 146 mg of a colourless syrup (**37**/**38**) and R_f 0.16: 65 mg (16%) of crystals (**39**). Prep. HPLC (*Dupont Zorbax-Sil, Q*, 4 ml/min, detection at 254 nm) of **37**/**38** afforded the pure products.

Data of **37**. 59 mg (12%) as syrup; t_R (*Q*): 42 min; $[\alpha]_D^{25}$ = +79.6° (*c* = 0.53, $CHCl_3$). IR: 3422*m*, 3260 (br.), 3140*w*, 3085*w*, 3062*w*, 3035*w*, 3002*m*, 2909*w*, 2870*m*, 1952*w*, 1875*w*, 1820*w*, 1720 (sh), 1711*s*, 1603*w*, 1495*m*, 1460 (sh), 1452*s*, 1429*m*, 1375 (sh), 1366*m*, 1350 (sh), 1300 (br.), 1220 (br.), 1155 (sh), 1210 (sh), 1195*s*, 1075 (sh), 1028 (sh), 1000 (sh), 910*w*, 689*m*, 670 (br.). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36–7.16 (*m*, 20 arom. H); 6.63 (*d*, *J* = 6, NH); 5.00 (*dt*, *J* = 10, 3, 3, H–C(5)); 4.82–4.38 (*m*, 8 benzyl. H); 4.58 (*t*, *J* = 6, 5, H–C(2)); 3.94 (*dd*, *J* = 10, 2, H–C(4)); 3.84 (*dd*, *J* = 5, 2, H–C(3)); 3.76 (*d*, *J* = 3, 2 H–C(6)). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 157.5 (*s*, C(1)); 137.9, 137.5, 137.2, 137.0 (4*s*, 4 arom. C); 128.3, 128.2, 127.7, 127.7, 127.6, 127.4, 127.3 (7*d*, 20 arom. C); 81.6 (*d*); 78.3 (*d*); 77.9 (*d*); 76.6 (*d*); 73.5 (*t*); 72.5 (*t*); 71.8 (*t*); 69.6 (*t*); 69.1 (*t*). EI-MS (35 eV): 554 (1, $M^+ + 1$), 553 (1, M^+), 463 (2), 462 (3), 448 (2), 447 (2), 446 (4), 445 (3), 420 (1), 419 (3), 418 (2), 417 (2), 416 (6), 392 (2), 391 (2), 390 (3), 389 (4), 374 (3), 360 (2), 359 (3), 357 (3), 356 (13), 355 (20), 354 (75), 339 (4), 326 (5), 324 (9), 312 (10), 311 (61), 310 (24), 300 (8), 296 (14), 295 (13), 294 (54), 283 (50), 280 (34), 271 (33), 255 (29), 252 (100), 248 (44), 237 (71). Anal. calc. for $C_{34}H_{35}NO_6$ (553.655): C 73.76, H 6.37, N 2.53; found: C 73.74, H 6.40, N 2.65.

Data of **38**. 54 mg (11%); m.p. 103–104° (Et_2O/hexane); t_R (*Q*): 34 min; $[\alpha]_D^{25}$ = −9.3° (*c* = 1.34, $CHCl_3$). IR: 3419*m*, 3260 (br.), 3090*w*, 3065*m*, 3030 (sh), 3005*m*, 2920 (br.), 2875*m*, 1952*w*, 1875*w*, 1810*w*, 1736 (sh), 1722*s*, 1602*w*, 1583*w*, 1494*m*, 1452*s*, 1400 (sh), 1390*m*, 1373*m*, 1340 (sh), 1327*m*, 1276*m*, 1260 (sh), 1220 (br.), 1163*m*, 1095*s*, 1070 (sh), 1052*s*, 1028*s*, 990 (sh), 911*m*, 690*m*, 670 (br.). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36–7.12 (*m*, 20 arom. H); 5.99 (*d*, *J* = 4.7, NH); 4.79–4.52 (*m*, 8 benzyl. H); 4.54 (*dd*, *J* = 4.7, 2.1, H–C(2)); 4.17 (*ddd*, *J* = 10.0, 4.0, 2.0, H–C(5)); 4.12 (*dd*, *J* = 10.0, 6.9, H–C(4)); 3.88, 3.81 (*J* = 11.0, 4.0, 2.0, 2 H–C(6)), 3.63 (*dd*, *J* = 6.9, 2.1, H–C(3)). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 157.8 (*s*, C(1)); 137.9, 137.7, 136.6 (3*s*, 4 arom. C); 128.5, 128.3, 128.0, 127.9, 127.8, 127.7, 127.5 (7*d*, 20 arom. H); 81.9 (*d*); 81.1 (*d*); 80.1 (*d*); 75.3 (*d*); 74.6 (*t*); 73.7 (*t*); 73.4 (*t*); 70.4 (*t*); 69.4 (*t*). EI-MS: 356 (1), 355 (2), 354 (7), 311 (3), 310 (2), 294 (2), 283 (3), 280 (2), 255 (2), 254 (17), 253 (79), 248 (4), 227 (6), 205 (7), 204 (6), 202 (5), 197 (7), 191 (5), 182 (25), 181 (100), 163 (8), 133 (5), 132 (5), 115 (7), 109 (6), 108 (77), 107 (73), 105 (18). Anal. calc. for $C_{34}H_{35}NO_6$ (553.655): C 73.76, H 6.37, N 2.53; found: C 73.52, H 6.30, N 2.71.

Data of **39**. M.p. 134–135.5° (CH_2Cl_2/EtO/hexane); $[\alpha]_D^{25} = -35.0°$ ($c = 0.14$, $CHCl_3$). IR: 3545*m*, 3435*m*, 3110 (sh), 3090*w*, 3065*w*, 3030 (sh), 3005*m*, 2945 (sh), 2910 (sh), 2870*m*, 2830 (sh), 1903*w*, 1815*w*, 1735*s*, 1603 (sh), 1585*s*, 1522 (sh), 1497*m*, 1465 (sh), 1452*s*, 1371*s*, 1322*s*, 1272*w*, 1220 (br.), 1103*s*, 1072*s*, 1038 (sh), 1029*m*, 990 (sh), 920*w*, 855*w*, 692*m*, 670 (br.). ^{1}H-NMR (200 MHz, $CDCl_3$): 9.63 (*d*, $J = 1.3$, CHO); 7.38–7.14 (*m*, 15 arom. H); 5.17 (*m*, $J = 7.2, 4.2, 3.2$, H–C(4)); 4.72–4.44 (*m*, 8 H); 4.21 (*dd*, $J = 7.1, 3.3$, H–C(3)); 3.93 (*dd*, $J = 3.3, 1.3$, H–C(2)); 3.85, 3.79 ($J = 10.7, 4.2, 3.2$, 2 H–C(6)). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 190.2 (*s*, CHO); 148.4 (OCON); 132.2, 131.5, 131.2 (3*s*, 3 arom. C); 123.6–122.7 (*m*, 15 arom. C); 82.2 (*d*); 77.2 (*d*); 74.5, 74.0, 73.8 (3*d*, 3 benzyl. C); 72.8 (*d*); 69.1 (*t*, C(5)). Anal. calc. for $C_{27}H_{29}NO_6$ (463.530): C 69.96, H 6.31, N 3.02; found: C 69.73, H 6.34, N 2.84.

17. *2-Acetamido-2-deoxy-*D*-glucono-1,4-lactone* (**40**). A soln. of **7a** (1 g, 4.3 mmol) and TsOH (820 mg, 1 equiv.) in DMSO (20 ml) was stirred for 3 h at 110°. The mixture was evaporated under high vacuum. MPLC (100 g/*A*) of the residue afforded **40** (574 mg, 61%) as yellow syrup. $R_f(A)$ 0.41. IR (KBr): 3400 (br.), 3300 (sh), 3100 (sh), 2940*w*, 2900 (sh), 1780*s*, 1660*s*, 1545*s*, 1430 (br.), 1375*m*, 1310 (br.), 1215 (sh), 1195*s*, 1165 (sh), 1135*m*, 1115*w*, 1090 (br.), 1040*s*, 1020*s*. FAB-MS: 277, 255, 242 ($M^+ + 23$), 220 (M^+), 114, 93.

18. *3-Acetamido-5-acetoxymethyl-2*H*-pyran-2-one Oxime* (**41**) *and 3-Acetamido-5-acetoxymethyl-2*H*-pyran-2-one* (**42**). A soln. of **8c** (360 mg, 1 mmol) and TsOH (1 equiv.) in DMSO (4 ml) was stirred at 70° for 5 h. The dark brown mixture was poured into CH_2Cl_2 and worked up as usual (CH_2Cl_2, 1M $NaHCO_3$). FC (22 g/*V*) of the residue afforded **42** ($R_f(V)$ 0.26, 67 mg; 27%) as crystals (m.p. 117°; from CH_2Cl_2/Et_2O/hexane) and **41** ($R_f(V)$ 0.11, 73 mg, 31%) as crystals (m.p. 131–132°; from CH_2Cl_2/Et_2O/hexane).

Data of **41**. UV (EtOH): 328 (6300), 242 (14500). IR: 3575*s*, 3460 (sh), 3390*s*, 3120*w*, 3090*w*, 3030*w*, 3000*m*, 2950 (sh), 1742*s*, 1700*s*, 1677*s*, 1621*s*, 1585*m*, 1515*s*, 1447 (sh), 1436*m*, 1390 (sh), 1368*s*, 1342*m*, 1329*s*, 1220 (br.), 1167*s*, 1072*m*, 1065*m*, 1026*s*, 972*s*, 960*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.68 (br., NH); 7.46 (*d*, $J = 7.3$, 1 H); 6.50 (br., OH); 5.93 (*d*, $J = 7.3$, 1 H); 4.77 (*s*, 2 H–C(6)); 2.15, 2.12 (2*s*, 2 CH_3). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 170.4 (*s*); 169.1 (*s*); 147.2 (*s*); 147.0 (*s*); 123.6 (*s*); 111.1 (*d*); 104.8 (*d*); 61.9 (*t*); 24.6, 20.7 (2*q*, 2 CH_3). CI-MS: 241 ($M^+ + 1$). Anal. calc. for $C_{10}H_{12}N_2O_5$ (240.215): C 50.00, H 5.04, N 11.66; found: C 50.25, H 4.93, N 11.45.

Data of **42**. UV (EtOH): 310 (11700), 243 (6300). IR: 3395*s*, 3340 (sh), 3090*m*, 3030*m*, 3000*m*, 2940 (sh), 1745*s*, 1720*s*, 1690*s*, 1655*s*, 1631*m*, 1510*s*, 1450*m*, 1435*m*, 1370*s*, 1345*s*, 1220 (br.), 1132*m*, 1080*m*, 1065*w*, 1030*s*, 970*m*, 930*m*, 830*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.23 (*d*, $J = 7.3$, 1 H); 8.01 (br., NH); 6.34 (*d*, $J = 7.3$, 1 H); 4.84 (*s*, 2 H–C(6)); 2.21, 2.13 (2*s*, 2 CH_3). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 169.9 (*s*); 169.3 (*s*); 158.9 (*s*); 150.3 (*s*); 125.1 (*s*); 122.4 (*d*); 106.3 (*d*); 61.5 (*t*); 24.5, 20.6 (2*q*, 2 CH_3). EI-MS: 225 (10, M^+), 183 (36), 141 (30), 124 (19), 96 (26), 43 (100). Anal. calc. for $C_{10}H_{11}NO_5$ (225.200): C 53.33, H 4.92, N 6.22; found: C 53.58, H 4.86, N 6.02.

19. *Tris[(2,3,4,6-tetra-*O*-acetyl-*D*-glucopyranosylidene)amino] Phosphate* (**43**) *and Bis[(2,3,4,6-tetra-*O*-acetyl-*D*-glucopyranosylidene)amino] Phosphochloridate* (**44**). To a stirred soln. of **2c** (54.9 mg, 0.15 mmol) in CH_2Cl_2 was added PCl_5 (38 mg, 1.2 mol-equiv.). After 2 min, the starting material had disappeared and H_2O (1 ml) was added. After 1 h, the mixture was worked up as usual (CH_2Cl_2/1M K_2CO_3). FC (6.2 g/*O*) afforded two fractions.

Data of **43**. $R_f(D)$ 0.10; syrup; 23 mg (41%). IR: 3030 (sh), 3005*m*, 2965*m*, 2940 (sh), 1760*s*, 1663*m*, 1659 (sh), 1447 (sh), 1428*m*, 1387 (sh), 1370*s*, 1300 (sh), 1275 (sh), 1220 (br.), 1100*m*, 1065 (sh), 1042*s*, 1008*m*, 930 (sh), 860*m*, 632 (br.). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.54 (*dd*, $J = 4.0, 0.4$, H–C(2)); 5.28 (*dd*, $J = 5.0, 4.0$, H–C(3)); 5.22 (*dd*, $J = 9.5, 5.0$, H–C(4)); 4.68 (*dt*, $J = 9.5, 3.9, 3.0$, H–C(5)); 4.50, 4.34 ($J = 13.0, 3.9, 3.0$, H–C(6)); 2.19, 2.16, 2.13, 2.12 (4*s*, 4 CH_3). EI-MS: 404 (1), 403 (1), 363 (1), 362 (1), 361 (3), 242 (3), 241 (2), 223 (18), 199 (13), 182 (7), 181 (72), 180 (20), 151 (20), 150 (12), 149 (16), 126 (22), 112 (9), 97 (6), 86 (8), 85 (7), 84 (23), 81 (17), 67 (23), 60 (100), 55 (8), 53 (13).

Data of **44**. $R_f(D)$ 0.27; syrup; 17 mg (31%). IR: 3020*m*, 2990 (sh), 1755*s*, 1705 (sh), 1659*m*, 1440 (sh), 1428*m*, 1370*s*, 1300*s*, 1240*s*, 1220 (br.), 1097*m*, 1062 (sh), 1043*s*, 1007*m*, 985 (sh), 958 (sh), 930 (br.), 850 (br.), 632*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.52 (*d*, $J = 4$, H–C(2)); 5.26 (*t*, $J = 4.5, 4$, H–C(3)); 5.20, 5.18 (2*dd*, $J = 9.5, 4.5$, 2 sets of H–C(4)); 4.69 (*ddd*, $J = 9.5, 7, 3.2$, H–C(5)); 4.36, 4.32 ($J = 3.2$, 2 H–C(6)); 2.20, 2.16, 2.15, 2.13 (4*s*, 4 CH_3). EI-MS: 802 ($M^+ - 1$); 779 (1); 767 (1, $M^+ - Cl$), 743 (1), 699 (1), 460 (1), 361 (2), 301 (1), 300 (1), 242 (3), 223 (5), 199 (5), 187 (3), 182 (3), 181 (20), 180 (6), 164 (7), 156 (6), 155 (7), 128 (11), 126 (10), 115 (13), 97 (12), 96 (12), 85 (21), 84 (15), 67 (18), 60 (100).

20. *(2,3,4,6-Tetra-*O*-acetyl-*D*-glucopyranosylidene)amino Methanesulfonate* (**45**). To a soln. of **2c** (146 mg, 0.4 mmol) and Et_3N (135 µl, 2.4 equiv.) in CH_2Cl_2 (5 ml) was added MsCl (375 µl, 1.2 equiv.). After 3 min, the mixture was evaporated *i.v.* and worked up as usual (CH_2Cl_2/1M $NaHCO_3$) FC (22 g/*C*) of the residue afforded **45** (132 mg, 74%) as syrup. $R_f(C)$ 0.25; $[\alpha]_D^{25} = +59.5°$ ($c = 3.0$, $CHCl_3$). IR: 3020*m*, 2960*w*, 2940 (sh), 1755*s*, 1665*m*, 1412*w*, 1372*s*, 1326*m*, 1235*s*, 1220 (br.), 1180*s*, 1095 (sh), 1060 (sh), 1043*s*, 969*s*, 867*m*, 837*s*. ^{1}H-NMR (200 MHz, $CDCl_3$):

5.51 (*dd*, *J* = 3.7, 0.7, H–C(2)); 5.23 (*dd*, *J* = 4.7, 3.7, H–C(3)); 5.18 (*ddd*, *J* = 9.8, 4.7, 0.7, H–C(4)); 4.68 (*ddd*, *J* = 9.8, 4.0, 2.8, H–C(5)); 4.43, 4.29 (*J* = 12.8, 4.0, 2.8, 2 H–C(6)); 3.15 (*s*, CH_3S); 2.19, 2.14, 2.12, 2.10 (4*s*, 4 CH_3). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 170.2, 168.8, 168.7, 167.4 (4*s*, 4 CH_3CO); 154.5 (*s*, C(1)); 75.3 (*d*); 71.1 (*d*); 68.1 (*d*); 66.7 (*d*); 61.0 (*t*); 36.0 (*s*, CH_3S); 20.4, 20.3 (*m*). CI-MS: 440 ($M^+ + 1$). Anal. calc. for $C_{15}H_{21}NO_{12}S$ (439.228): C 41.02, H 4.82, N 3.19; found: C 41.28, H 4.65, N 3.32.

21. *(2,3,4,6-Tetra-*O*-acetyl-*D*-glucopyranosylidene)amino Trifluormethanesulfonate* (**46**). A stirred soln. of **2c** (153 mg, 0.42 mmol) and pyridine (340 µl) in CH_2Cl_2 (4 ml) was cooled to −78° and treated with trifluoromethanesulfonic anhydride (209 µl, 10 equiv.). After 3 min, the starting material had disappeared, and the mixture was worked up as usual (CH_2Cl_2). FC (8.5 g/*F*) afforded **46** (185 mg, 89%) as colourless crystals. An anal. sample was recrystallized from CH_2Cl/Et_2O/hexane, m.p. 92–93°. $R_f(C)$ 0.48; $[\alpha]_D^{25} = +58.7°$ (*c* = 6.78, $CHCl_3$). IR: 3030*m*, 2960*m*, 2925*w*, 2850*w*, 1762*s*, 1652*m*, 1425*s*, 1369*s*, 1220 (br.), 1138*s*, 1061 (sh), 1043*s*, 1010 (sh), 950*w*, 931*w*, 845 (br.). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.53 (*d*, *J* = 4.0, H–C(2)); 5.29 (*t*, *J* = 4.5, 4.0, H–C(3)); 5.19 (*dd*, *J* = 9.5, 4.5, H–C(4)); 4.73 (*ddd*, *J* = 9.5, 3.5, 2.8, H–C(5)); 4.41, 4.39 (*J* = 3.5, 2.8, 2 H–C(6)); 2.19, 2.14, 2.12, 2.11 (4*s*, 4 CH_3). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 170.1, 168.7, 168.6, 167.6 (4*s*, 4 CH_3CO); 157.7 (*s*, C(1)); 118.6 (*q*, *J*(C,F) = 327, CF_3); 76.4, 70.7, 68.0, 66.4 (4*d*, C(2), C(3), C(4), C(5)); 61.0 (*t*, C(6)); 20.4 (*q*, 4 CH_3). EI-MS: 360 (6, $M^+ - SO_2CF_3$), 332 (3), 331 (6), 303 (5), 302 (21), 301 (1), 288 (2), 287 (2), 285 (2), 284 (7), 272 (4), 271 (1), 260 (5), 259 (4), 258 (3), 245 (3), 244 (4), 243 (22), 242 (63), 200 (23), 170 (32), 157 (49), 145 (43), 141 (38), 140 (62), 128 (82), 127 (34), 115 (100), 113 (23), 112 (31), 103 (70), 102 (19), 99 (28), 98 (33), 97 (37), 95 (25), 86 (51), 85 (91), 81 (54), 73 (49), 70 (18), 69 (83), 68 (38), 64 (26), 61 (20), 60 (76), 55 (28). Anal. calc. for $C_{15}H_{18}F_3NO_{12}S$ (493.358): C 36.52, H 3.68, N 2.84; found: C 36.81, H 3.74, N 2.70.

22. *D-Gluconhydroximo-1,5-lactone 1-*N*,2,3,4,6-Pentabenzoate* (**47**). To an ice cold stirred suspension of **2a** (97 mg, 0.5 mmol) in pyridine (20 ml) was added dropwise benzoyl chloride (870 µl, 7.5 mmol). After 30 min, the reaction was complete, and the mixture was evaporated in high vacuum. Usual workup (CH_2Cl_2/1M $NaHCO_3$) gave 335 mg (94%) of colourless crystals; m.p. 169–170° (CH_2Cl_2/Et_2O/hexane); $R_f(C)$ 0.60; $[\alpha]_D^{25} = +58.4°$ (*c* = 1.12, $CHCl_3$). IR: 3090*w*, 3070*w*, 3030*m*, 2970 (sh), 1970*w*, 1920*w*, 1735*s*, 1662*s*, 1655 (sh), 1602*m*, 1587*w*, 1481*w*, 1451*s*, 1380 (br.), 1317*m*, 1250 (br.), 1178*m*, 1100 (sh), 1088*s*, 1068*s*, 1035*s*, 915 (br.), 850*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.20–7.20 (*m*, 25 arom. H); 6.17 (*dd*, *J* = 4.0, 0.8, H–C(2)); 5.92 (*t*, *J* = 4.0, 3.0, H–C(3)); 5.84 (*ddd*, *J* = 9.0, 3.0, 0.7, H–C(4)); 5.16 (*ddd*, *J* = 9.0, 5.5, 3.0, H–C(5)); 4.98, 4.70 (*J* = 12.5, 5.5, 3.0, 2 H–C(6)). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 165.7, 164.4, 164.2, 163.7, 162.9 (5*s*, 5 Ph*C*); 154.8 (*s*, C(1)); 133.9, 133.7, 133.2 (3*s*, 5 arom. C); 130.0, 129.7, 129.6, 129.2, 129.1, 128.6, 128.3, 128.1, 127.8, 127.7 (10*d*, 25 arom. C); 76.1 (*d*); 70.3 (*d*); 68.5 (*d*); 67.3 (*d*); 62.6 (*t*). EI-MS: 715 (1, $M^+ + 1$), 714 (2, M^+), 713 (3), 593 (1), 592 (1), 471 (1), 472 (2), 365 (1), 364 (1), 349 (1), 348 (12), 347 (61), 243 (8), 242 (56), 199 (1), 198 (6), 188 (3), 187 (1), 182 (3), 181 (3), 123 (41), 122 (100), 115 (21), 106 (82), 105 (100), 104 (10), 103 (12), 94 (11), 77 (100). Anal. calc. for $C_{43}H_{31}NO_{11}$ (713.695): C 69.00, H 4.38, N 1.96; found: C 68.97, H 4.38, N 2.12.

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