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Nitrosation of Sugar Oximes: Preparation of 2-Glycosyl-1-hydroxydiazene-2-oxides

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Abstract: Oximes of glucose, xylose, lactose, fructose, and mannose have been prepared. Nitrosation of the oximes of glucose, xylose, and lactose with $NaNO_2$/HCl afforded 2-(β-glycopyranosyl)-1-hydroxydiazene-2-oxides, which were isolated as salts **13**, **22**, and **28**. Nitrosation of fructose oxime **29** furnished fructose, whereas nitrosation of mannose oxime **30** with $NaNO_2$/HCl afforded the 1-hydroxy-2-(β-D-mannopyranosyl)diazene-2-oxide **32**, from which the *p*-anisidinium salt **31** and the sodium salt **33** were prepared. However, nitrosation of **30** with isopentyl nitrite in aqueous solutions of CsOH or KOH resulted in the formation of the 2-(α-D-mannofuranosyl)-1-hydroxydiazene-2-oxide salts **34** and **35**, respectively. Methylation of the ammonium 2-(β-D-glucopyranosyl)-1-hydroxydiazene-2-oxide **13** yielded the 1-methoxy compound, which was benzoylated to afford the tetra-*O*-benzoate **14a**, the structure of which was confirmed by X-ray diffraction analysis. From the glucose *O*-methyloximes **15** and **16** the *N*-methoxy-*N*-nitroso-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine **18** was prepared. The structure of this compound was confirmed by X-ray diffraction analysis. Treatment of acetobromoglucose with cupferron furnished the 1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-2-phenyldiazene-2-oxide **20**.

Keywords: carbohydrates · glycosyl oximes · nitrosation · NO donors · X-ray diffraction

Introduction

Substituted diazene-1-olate-2-oxides, such as cupferron (**1**), are known to release nitric oxide under physiological conditions.[1–3] The endogenously formed nitric oxide displays a broad variety of bioregulatory activities, including vasodilation, cardiovascular effects, inhibition of platelet aggregation, and inflammatory and antileukaemic activities, together with influences on cognitive processes, on uterine relaxation, on impotency, and on the immune system.[1–13] In 1998 Furchgott, Ignarro, and Murad were honored with the Nobel prize for their discoveries of the multiple bioactivities of NO. A few diazene-1-olate-2-oxides are known as natural products, for instance (*S*)-alanosine (**2**),[14–21] (*S*)-homoalanosine (**3**),[22] (*S*)-dopastin (**4**),[23,24] and (*S*)-fragin (**5**).[25,26]

During recent years, numerous diazene-1-olate-2-oxides (also referred to as diazeniumdiolates[2]) have been prepared and tested for medicinal applications.[11,27–30] The main problem is to develop NO donors capable of providing the required quantities of NO to the specific tissue of need without disturbing other NO-sensitive portions of the anatomy. Thus, Wang and co-workers have prepared glycosylated hydroxydiazene-2-oxides such as the glucosyl derivative **6** and more recently the *N*-acetylneuraminic acid derivative **7** (to target influenza viruses) in the expectation that such glycosylated compounds should easily be transported into cells because of the presence of sugar transporters in the cell membranes.[10,31,32] Before that, Vasella et al. had synthesized the glycosides **8** and **9** by oxidation of diisopropylidenemannose oxime or tetra-*O*-benzylglucosylamine, respectively.[33] The structure of compound **8** was confirmed by X-ray analysis.

In this article we describe the preparations and two X-ray diffraction analyses of N2-glycosylated diazene-1-olate-2-oxides: to the best of our knowledge, and with the exception of compounds **8** and **9**, a hitherto unknown class of diazeniumdiolates. Building on the work by Wang et al.,[10,31,32] we also prepared the new cupferron derivative **20** (Scheme 1).

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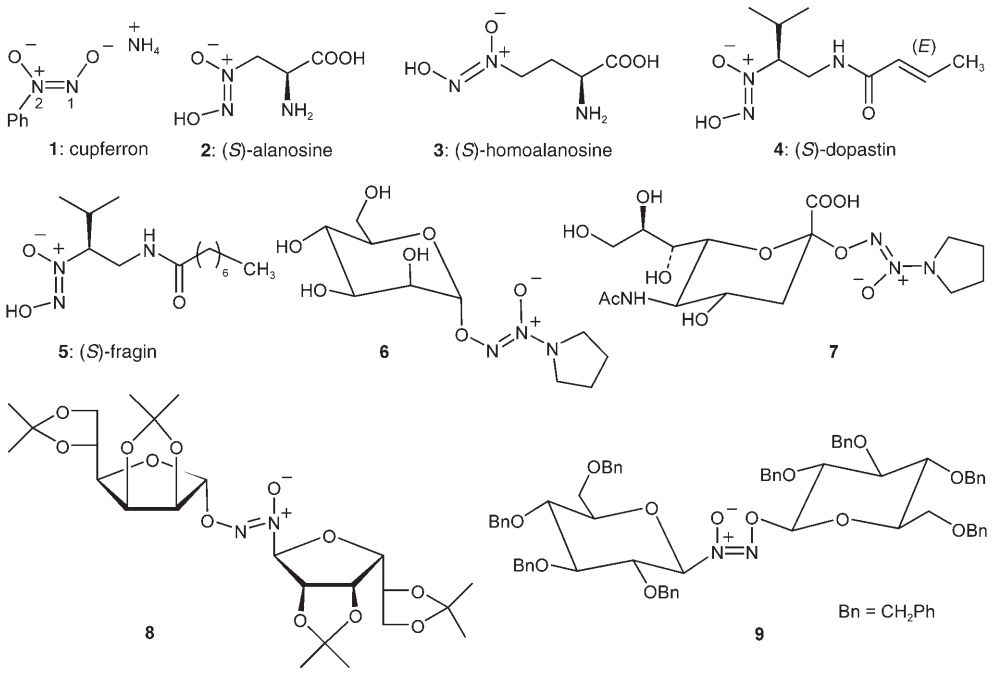


Results and Discussion

Treatment of aldoses and ketoses with hydroxylamine affords open-chain oximes. An exception is glucose, from which the *E*- and *Z*-open-chain oximes **10** and **11** and the *N*-β-D-glucopyranosylhydroxylamine **12** have been prepared (Scheme 1).[34–38] Recently, the synthesis of a cyclic *N*-β-D-xylofuranosylhydroxylamine has been reported.[39] We prepared the crystalline compound **12** (yield 82%) by stirring glucose with hydroxylamine in dry methanol at 20–25°C. Under similar conditions we obtained high yields of crystalline open-chain oximes from D-xylose, D-lactose, D-fructose, and D-mannose.

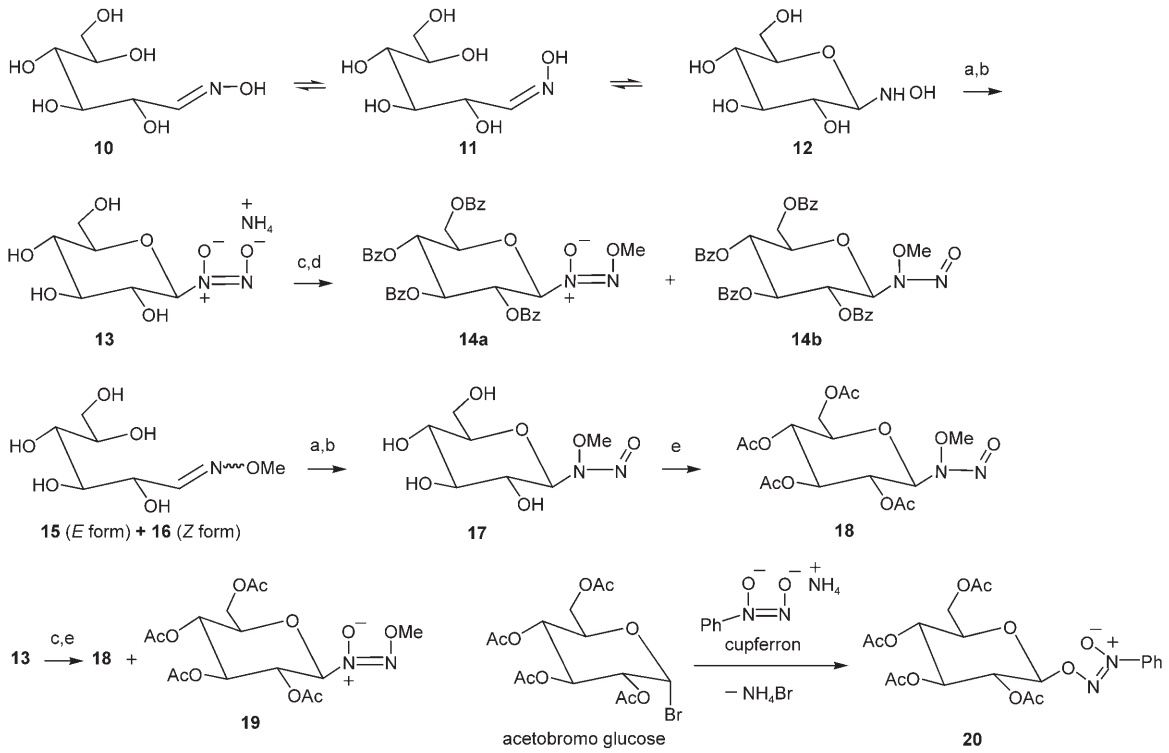
Nitrosations of N-monosubstituted hydroxylamines to produce 2-substituted diazene-1-olate-2-oxides have been known for more than 100 years.[40–42] Treatment of the hydroxylamine **12** with $NaNO_2$ in dilute hydrochloric acid afforded—after neutralization with ammonia—a solid consisting, according to the ^1H and ^{13}C NMR spectra (Table 2, below), of a mixture of ammonium 2-(β-D-glucopyranosyl)diazene-1-olate-2-oxide (**13**, 75%), α- and β-D-glucopyranose (6 and 15%), trace amounts of (*E*)- and (*Z*)-D-glucose oximes **10** and **11**, and traces of other sugars, which were not identified. Crystallization from methanol/water containing a small amount of NH_3 yielded pure compound **13** (yield 65%). The coupling constants—$J_{H1,H2}$ = 9.0 Hz and $J_{H3,H4} = J_{H4,H5} = 9.4$ Hz—are indicative of the β-pyranosyl structure. The UV absorption—$\lambda_{max} = 254$ nm ($\varepsilon = 9816\,M^{-1}cm^{-1}$)—is characteristic of diazene-1-olate-2-oxides.[10,33,43–48]

The salt **13** proved to be quite stable: unlike other 2-substituted diazene-1-olates-2-oxides, which are known to eliminate NO or N_2O, compound **13** can be stored at room temperature over months without decomposition. The ^1H NMR spectrum of a solution of **13** in D_2O remained unchanged after the sample had been boiled for three minutes. However, attempts to acetylate compound **13** with acetic anhydride in pyridine resulted in penta-*O*-acetyl-D-glucopyranose.[49–51]

The small crystals of **13** were not appropriate for single-crystal X-ray diffraction analysis. Therefore we prepared some derivatives to verify the proposed structure of **13**.

Methylation of **13** with dimethyl sulfate followed by benzoylation furnished a crystalline mixture of the 1-methoxydiazene-2-oxide **14a** and the *N*-methoxy-*N*-nitrosohydroxylamine **14b**. Recrystallization afforded needles of pure **14a** suitable for X-ray diffraction analysis. Compound **14a** crystallizes from ethanol in the orthorhombic space group $P2_12_12_1$ ($a = 9.371(3)$, $b = 16.733(3)$, $c = 21.421(4)$ Å). The final R (for $F^2 \geq 2\sigma(F^2)$) was 0.0601 and $wR = 0.1841$ (all reflections). A stereoscopic view of compound **14a** is shown in Figure 1, and selected bond lengths and angles are given in Table 1.

To support the structure of compound **14b**, glucose was treated with *O*-methylhydroxylamine to yield a mixture of the open-chain (*E*)- and (*Z*)-glucose-*O*-methyloximes **15** and **16**.[52–54] Nitrosation resulted in the formation of the cyclic *N*-nitroso-*O*-methylhydroxylamine **17** as a yellow syrup, and this was acetylated to furnish the crystalline tetraacetate **18** (Scheme 1). The constitution of this compound was also confirmed by X-ray diffraction analysis.[55] Compound **18** crystallizes from THF/pentane in the orthorhombic space group $P2_12_12_1$ ($a = 5.723(1)$, $b = 17.650(3)$, $c = 19.666(3)$ Å). The final R was 0.0479 (for $F^2 \geq 2\sigma(F^2)$) and $wR = 0.1311$ (for all reflections). A stereoscopic plot of compound **18** is shown in Figure 1 and selected bond lengths and angles are given in Table 1.



Scheme 1. Reactions of glucose oximes with NO^+ and preparation of the cupferron derivative **20**. Structural studies by X-ray crystallography are reported for compounds **14a** and **18**. a) $HCl/H_2O + NaNO_2$. b) NH_3/H_2O. c) $Me_2SO_4/NaHCO_3/H_2O$. d) BzCl/pyridine. e) Ac_2O/pyridine.

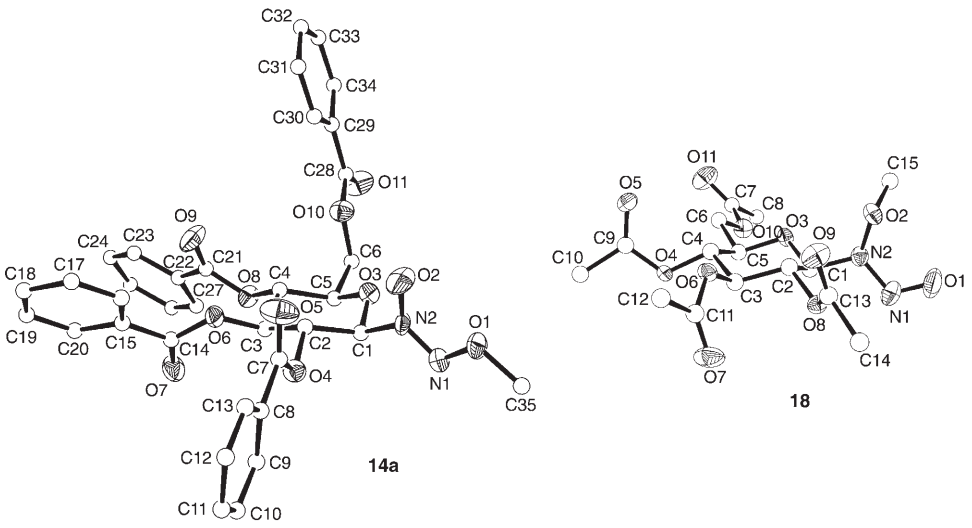


Figure 1. Molecular structure of **14a** and **18** in the crystal (displacement ellipsoids 50%; C atoms with arbitrary radii; H atoms omitted for clarity).

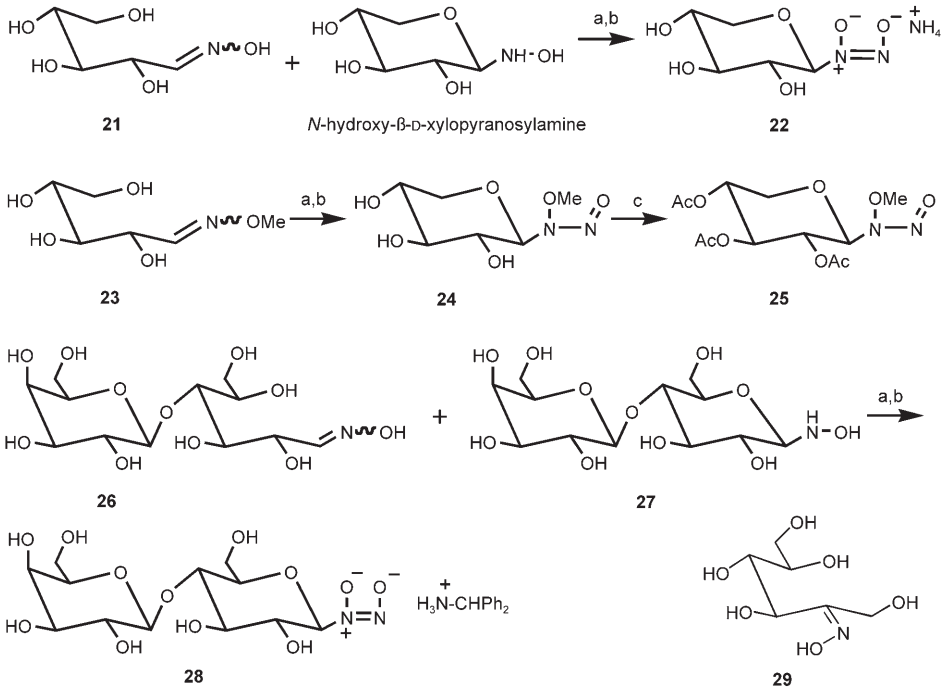
Methylation of compound **13** and subsequent acetylation afforded a mixture of the isomers **18** and **19**, which were separated by crystallization and by column chromatography.

The crystalline cupferron derivative **20** (Scheme 1) was obtained in moderate yield (≈40%) by treatment of α-acetobromoglucose with cupferron. In water, compound **20** hydrolyzed within a few days to mixtures of α- and β-2,3,4,6-tetra-*O*-acetyl-D-glucopyranose[55] and azoxybenzene.[56]

After the successful nitrosation of hydroxylamine **12** we were interested in how open-chain sugar oximes would react with NO^+. Xylose has been reported to react with hydroxylamine to form an equilibrium mixture of the *E*- and *Z*-open-chain oximes and the *N*-hydroxy-β-D-xylopyranosylamine (ratio about 80:18:3).[57,58] From D-xylose we obtained a similar noncrystalline mixture of the *E*- and *Z*-oximes (**21**) and the *N*-hydroxy-β-D-pyranosylamine (Scheme 2). The ^1H NMR spectrum of a solution of mixture **21** in D_2O did not show any change over many days. Treatment of an aqueous solution of this mixture with $NaNO_2$/HCl and then NH_3 yielded the ammonium salt **22** (77%) contaminated with α- and β-xylopyranose (≈8% each) together with small amounts of other sugars (not identified). Crystallization from H_2O/MeOH afforded the pure salt **22**, the constitution of which was characterized by elemental analysis and by NMR and UV spectra. Compound **22** is less stable than the glucose derivative **13**. At 23°C the crystals turned brown in the course of a few weeks, whereas in HCl

Table 1. Selected bond lengths [Å] and angles [°] of compounds **14a** and **18**.

	Bond length		Bond angle		Torsional angle	
14a	C1–C2	1.523(8)	C1-N2-O2	119.1(5)	C1-N2-N1-O1	179.3(4)
	C1–O3	1.406(7)	C1-N2-N1	115.4(5)	C2-C1-N2-O2	−50.7(7)
	C1–N2	1.469(7)	O2-N2-N1	125.5(5)	C2-C1-N2-N1	129.3(5)
	N2–N1	1.269(6)	N2-N1-O1	108.0(5)	O3-C1-N2-O2	67.8(6)
	N2–O2	1.264(6)	N1-O1-C35	108.9(5)	O3-C1-N2-N1	−112.2(5)
	N1–O1	1.363(6)			N2-N1-O1-C35	−176.6(5)
	O1–C35	1.438(8)			O2-N2-N1-O1	−0.7(8)
18	C1–C2	1.529(4)	C1-N2-O2	115.0(2)	C1-N2-N1-O1	−157.9(3)
	C1–O3	1.412(4)	C1-N2-N1	115.9(3)	C2-C1-N2-O2	−48.1(3)
	C1–N2	1.442(4)	O2-N2-N1	119.4(3)	C2-C1-N2-N1	97.9(3)
	N2–N1	1.356(4)	N2-N1-O1	113.8(3)	O3-C1-N2-O2	72.7(3)
	N2–O2	1.385(3)	N2-O2-C15	109.5(2)	O3-C1-N2-N1	−141.4(3)
	N1–O1	1.219(4)			O2-N2-N1-O1	−13.5(5)
	O2–C15	1.438(4)			N1-N2-O2-C15	97.2(3)
					C1-N2-O2-C15	−118.1(3)



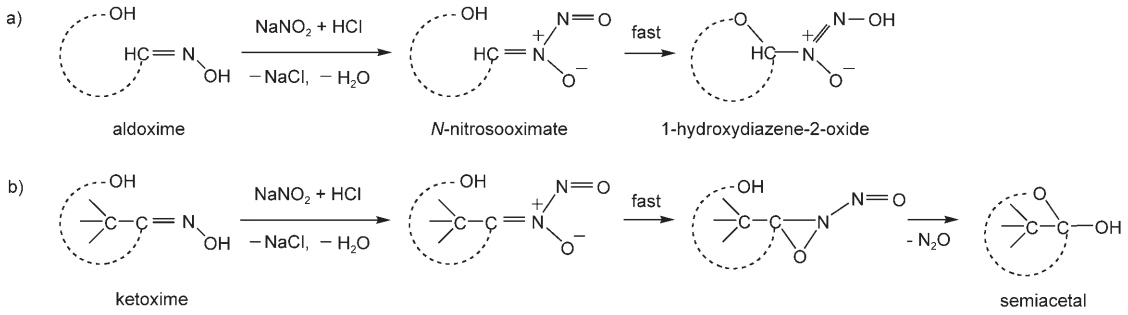
Scheme 2. Reactions of xylose, lactose, and fructose oximes with NO^+. a) $HCl/H_2O + NaNO_2$. b) $Ph_2CH–NH_2$. c) Ac_2O/pyridine.

(1 M) compound **22** decomposed into xylose within minutes. An explanation for the different stabilities of compounds **13** and **22** was offered by one of the referees: Paulsen has pointed out that removing one OR group (the 6-CH_2OH group of **13** to give **22**) increases the reactivity of the glycosyl donor, the reactivity correlating with the oxycarbenium cation stability.[59] The crystalline acetylated *N*-methoxy-*N*-nitrosoxylopyranosylamine **25** was prepared from compounds **23**[52–54] in the manner described for compound **18**.

We next studied the nitrosation of a disaccharide oxime. The preparation of lactose oxime has only been described once.[60] We found that treatment of D-lactose with hydroxylamine resulted in the formation of a crystalline mixture of the open-chain *E*- and *Z*-oximes **26** and the cyclic *N*-hydroxy-β-D-lactopyranosylamine **27** (ratio 10 min after dissolution in D_2O ≈0.3:1.0:0.01; Scheme 2). At 23 °C, the concentration of the hydroxylamine **27** increased slowly over 26 days. The final equilibrium of the *E*- and *Z*-oximes **26** and the hydroxylamine **27** reached a ratio of about 5.3:1.0:2.3. Nitrosation of the initial mixtures of compounds **26** and **27** with $NaNO_2$/HCl afforded (after neutralization with NH_3 or alternatively with $NaHCO_3$, $KHCO_3$, CsOH, pyridine, $BuNH_2$, 4-MeO-$C_6H_4NH_2$, or $Ph_2CH–NH_2$) the corresponding diazene-1-olate-2-oxides, of which the benzhydrylammonium salt **28** (yield 72%) proved to be the easiest to crystallize and to purify.

The observed slow cyclization of the open-chain oximes **26** to hydroxylamine **27** poses the question of the mechanism of the nitrosation. Pursuing the nitrosation of the mixture of (*E*)- and (*Z*)-**26**, containing only traces of hydroxylamine **27**, by using ^1H NMR showed that the formation of product **28** occurs much more rapidly (within seconds or at most within a few minutes) than the cyclizations of the open-chain oximes **26** (requiring days). Reactions between oximes and NO^+ are well documented,[61–65] and reaction mechanisms have been studied.[66–72] In view of mechanisms suggested by Freeman,[71] we propose that not only hydroxylamine **27** but also the open-chain *E*- and *Z*-oximes **26** undergo fast reactions with NO^+.

Reactions between ketoximes and NO^+ result in the formation of carbonyl compounds plus N_2O.[71] Less frequently, carbonyl products are also formed from aldoximes on nitrosation. The reactions start with an electrophilic attack of NO^+ on the oxime nitrogen (Scheme 3). The resulting *N*-nitrosooxime splits off a proton to form a *N*-nitrosooximate. If there are OH groups in the molecule, the two subsequent competing reactions are probably directed by steric effects. Clearly, in the case of ketoximes the attack of the *N*-nitrosooximate-O^- ion on the C=N double bond is faster than



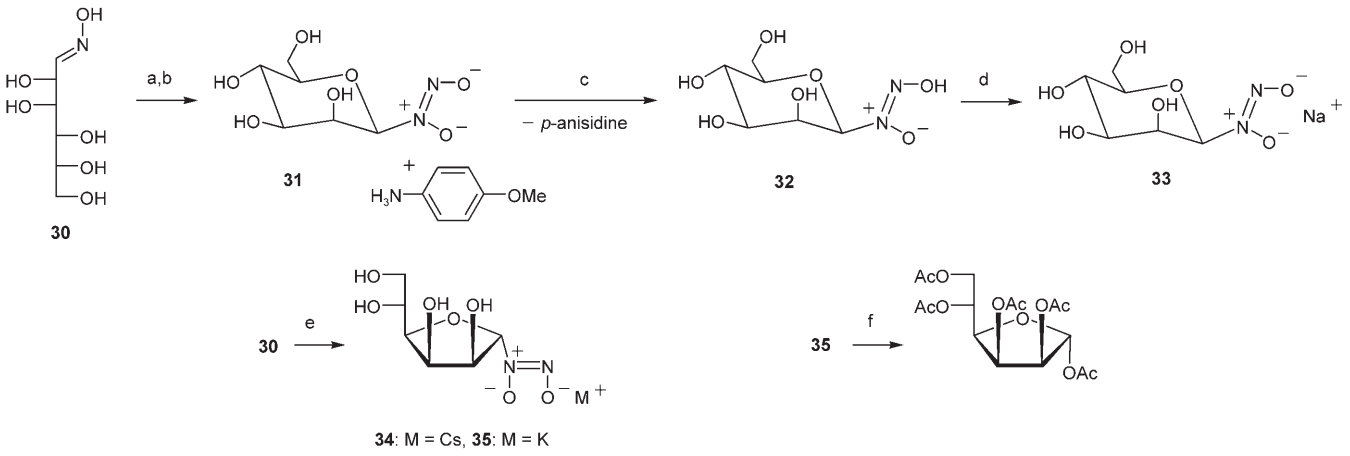
Scheme 3. Proposed nitrosation mechanisms for ω-hydroxyaldoximes and ω-hydroxyketoximes.

the intramolecular reaction with the OH group. The resulting oxaziridine undergoes intramolecular ring-opening with the OH group to form a semiacetal + N_2O (Scheme 3b). In the case of, for example, aldoximes (oximes of aldoses), on the other hand, the intramolecular attack of an OH group on the C=N double bond of the *N*-nitrosooximate to afford a 2-substituted 1-hydroxydiazene-2-oxide seems to be faster than the formation of a *N*-nitrosoxaziridine (Scheme 3a). Details of the mechanisms await further investigations.

To test whether ketoximes of carbohydrates would react with NO^+ according to Scheme 3b, we prepared D-fructose oxime (**29**).[73–75] We found that nitrosation of this open-chain oxime under diverse experimental conditions resulted in the exclusive formation of D-fructose, and so it seems unlikely that diazene-1-olate-2-oxides could be prepared from oximes of ketoses.

Finally, to study the influence of the configuration of the 2-OH group, we examined the nitrosation of D-mannose oxime (**30**; Scheme 4).[37,76–78] According to an X-ray structural analysis, compound **30** is an open-chain *E*-oxime.[77] We prepared mannose oxime **30** (yield 87%) from D-mannose in the manner described for compound **12**. NMR spectra (D_2O) of **30** showed a mixture ($E/Z = 1.0:0.1$) of the open-chain oximes, but no trace of a pyranosyl- or furanosylhydroxylamine. At 23°C the *E*/*Z* ratio of an aqueous solution of **30** did not change over several days.

Treatment of aqueous solutions of the oxime **30** with $NaNO_2$/HCl afforded (after neutralization with NH_3 or $NaHCO_3$ or $KHCO_3$) amorphous mixtures of 2-(D-mannopyranosyl)diazene-1-olate-2-oxides, mannose, and some unidentified mannose derivatives. We had problems in separating these mixtures, but neutralization with *p*-anisidine produced the solid *p*-anisidinium salt **31**, which was converted into the pure acid **32** plus *p*-anisidine simply by dissolution in THF/MeOH. To the best of our knowledge, 2-glycosyl-1-hydroxydiazene-2-oxides have not been reported in the literature until now. The large $J_{H3,H4}$ and $J_{H4,H5}$ coupling constants of almost 10 Hz are indicative of the pyranose structure of **32**. According to a report that $J_{H1,H2} < 1.5$ Hz for β-mannopyranoses and $J_{H1,H2} > 2.1$ Hz for α-mannopyranoses,[37] we tentatively assign β-configuration to the acid **32** ($J_{H1,H2} \approx 1.2$ Hz). Compound **32** is only moderately soluble in H_2O and rather sensitive to acid, so when the reaction time of the nitrosation of the mannose oxime at 0–5°C in dilute aqueous HCl was extended to more than 45 min, increasing amounts of mannose were formed. Furthermore, during ^{13}C NMR measurements of solutions of **32** in D_2O (about 10 h at 30°C) at least 2% of **32** was hydrolyzed to mannose.



Scheme 4. Reactions of mannose oxime with NO^+. a) $NaNO_2$/HCl. b) *p*-Anisidine. c) THF/MeOH. d) $NaHCO_3$. e) $Me_2CHCH_2CH_2$–ONO, H_2O, M^+OH^-. f) Ac_2O/pyridine, 5°C.

Neutralization of acid **32** with $NaHCO_3$ in H_2O afforded the crystalline and quite stable sodium salt **33**. Again, the large $J_{H3,H4}$ and $J_{H4,H5}$ coupling constants, of more than 9 Hz, and the small $J_{H1,H2}$ coupling of about 0.1 Hz are in agreement with the structure of a β-pyranose.

Nitrosations of nitrogen compounds have been carried out not only with $NaNO_2$ under acidic conditions but also with alkyl nitrites RO–NO in the presence of bases.[61,79] We found that nitrosations of D-mannose oxime (**30**) with isopentyl nitrite in aqueous solutions of CsOH or KOH resulted in the isolation of the cesium or potassium salts **34** and **35** of 1-hydroxy-2-(α-D-mannofuranosyl)diazene-2-oxide (Scheme 4). X-ray structural analyses to verify the anomeric configurations of these compounds are planned, but we have so far been unable to prepare suitable crystals, so the configurations of these compounds are still not absolutely certain, although the small coupling constants of 2–3 Hz between H3 and H4 and the larger couplings of 9 Hz between H4 and H5 in these compounds are consistent with corresponding coupling constants in other mannofuranoses.[80–82] The relatively high-field ^{13}C NMR shifts of 101.1 ppm for C1 in both **34** and **35** exclude the possibility of open-chain compounds (compare, for instance, the open-chain oximes **30**: (*E*)-C1 $\delta = 155.4$, (*Z*)-C1 $\delta = 155.0$ ppm; Table 2).[83] Support for the assignment of the α-configurations to compounds **34** and **35** is provided by the molecular rotations (**34**: $[M]_D^{23} = +281.3$ (H_2O) and **35**: $[M]_D^{23} = +283.6$ (H_2O)) and the large $^3J_{H1,H2}$ coupling constants of 6.6 Hz.[80,86] According to Hudson's isorotation rule, large positive molecular rotations point

Table 2. ^1H and ^{13}C data (also see the Experimental Section) of the diazene-2-glycosyl-1-olate-2-oxides (m = multiplet, *J* not determined).

δ [ppm]		*J* [Hz]		δ [ppm]		δ [ppm]		*J* [Hz]		δ [ppm]	
13[a]						**14a**[b]					
H1	5.29	$J_{1,2}$	9.0	C1	96.5	H1	5.73	$J_{1,2}$	9.0	C1	99.1
H2	≈3.93	$J_{2,3}$	m	C2	72.1	H2	6.19	$J_{2,3}$	9.5	C2	69.1
H3	≈3.65	$J_{3,4}$	9.4	C3	78.5	H3	6.06	$J_{3,4}$	9.8	C3	72.8
H4	3.51	$J_{4,5}$	9.4	C4	71.7	H4	5.83	$J_{4,5}$	9.8	C4	68.7
H5	≈3.65	$J_{5,6}$	m	C5	80.8	H5	≈4.42	$J_{5,6}$	5.3	C5	75.4
H6	3.77	$J_{5,6'}$	5.1	C6	63.2	H6	4.56	$J_{5,6'}$	3.0	C6	62.7
H6′	≈3.88	$J_{6,6'}$	12.5			H6′	4.68	$J_{6,6'}$	12.3		
14b[c]						**17**[a]					
H1	6.06	$J_{1,2}$	9.4	C1	89.5	H1	5.84	$J_{1,2}$	9.4	C1	94.1
H2	6.24	$J_{2,3}$	≈9.4	C2	≈68.4	H2	≈3.94	$J_{2,3}$	m	C2	71.7
H3	6.12	$J_{3,4}$	≈9.7	C3	≈74.1	H3	≈3.69	$J_{3,4}$	≈9.7	C3	78.7
H4	5.90	$J_{4,5}$	≈9.7	C4	≈69.4	H4	3.51	$J_{4,5}$	≈9.4	C4	71.6
H5	≈3.60	$J_{5,6}$	2.9	C5	≈75.0	H5	≈3.68	$J_{5,6}$	m	C5	81.1
H6	4.58	$J_{5,6'}$	4.6	C6	62.7	H6	≈3.92	$J_{5,6'}$	5.8	C6	63.2
H6′	≈3.88	$J_{6,6'}$	12.5			H6′	3.76	$J_{6,6'}$	12.5		
18[b]						**19**[b]					
H1	6.02	$J_{1,2}$	9.4	C1	89.0	H1	5.32	$J_{1,2}$	9.4	C1	94.7
H2	5.50	$J_{2,3}$	≈9.4	C2	67.3	H2	5.65	$J_{2,3}$	≈9.4	C2	68.4
H3	5.38	$J_{3,4}$	≈9.6	C3	73.2	H3	5.33	$J_{3,4}$	≈9.5	C3	72.7
H4	5.21	$J_{4,5}$	≈9.7	C4	67.6	H4	5.23	$J_{4,5}$	≈9.5	C4	67.2
H5	≈3.96	$J_{5,6}$	4.9	C5	74.5	H5	3.91	$J_{5,6}$	2.3	C5	75.0
H6	4.28	$J_{5,6'}$	2.0	C6	61.6	H6	4.19	$J_{5,6'}$	4.9	C6	61.5
H6′	4.22	$J_{6,6'}$	12.5			H6′	4.28	$J_{6,6'}$	12.6		
20[d]						**22**[a]					
H1	5.35	$J_{1,2}$	8.2	C1	100.9	H1	5.22	$J_{1,2}$	9.0	C1	97.2
H2	5.54	$J_{2,3}$	9.4	C2	69.4	H2	3.92	$J_{2,3}$	≈9.2	C2	72.0
H3	5.32	$J_{3,4}$	9.4	C3	72.9	H3	3.59	$J_{3,4}$	≈9.2	C3	78.7
H4	5.20	$J_{4,5}$	9.8	C4	67.8	H4	3.72	$J_{4,5e}$	5.5	C4	71.4
H5	≈3.66	$J_{5,6}$	4.7	C5	72.8	H5a	3.47	$J_{4,5a}$	10.9	C5	70.1
H6	4.23	$J_{5,6'}$	2.3	C6	61.5	H5e	4.07	$J_{5e,5a}$	≈11.1		
H6′	4.08	$J_{6,6'}$	12.5								
25[a]						**28**[a]					
H1	5.78	$J_{1,2}$	9.3	C1	94.7	H1	5.32	$J_{1,2}$	9.0	C1	96.4
H2	3.93	$J_{2,3}$	≈9.3	C2	71.7	H2	3.99	$J_{2,3}$	m	C2	71.8
H3	3.64	$J_{3,4}$	≈9.2	C3	78.9	H3	3.79	$J_{3,4}$	m	C3	78.1
H4	≈3.72	$J_{4,5a}$	≈11.0	C4	71.3	H4	–	$J_{4,5}$	m	C4	71.3
H5a	3.53	$J_{4,5e}$	5.3	C5	70.2	H5	–	$J_{5,6}$	m	C5	80.1
H5e	4.10	$J_{5a,5e}$	≈11.3			H6	–	$J_{5,6'}$	m	C6	62.6
32[a]						**33**[a]					
H1	5.58	$J_{1,2}$	1.2	C1	97.4	H1	5.37	$J_{1,2}$	≈0.1	C1	93.9
H2	4.47	$J_{2,3}$	3.1	C2	72.0	H2	4.43	$J_{2,3}$	2.3	C2	72.3
H3	≈3.82	$J_{3,4}$	≈9.6	C3	75.2	H3	≈3.77	$J_{3,4}$	≈9.4	C3	75.6
H4	3.69	$J_{4,5}$	≈9.7	C4	68.8	H4	3.74	$J_{4,5}$	≈9.2	C4	69.0
H5	≈3.60	$J_{5,6}$	2.3	C5	82.1	H5	3.58	$J_{5,6}$	≈2.3	C5	81.8
H6	3.97	$J_{5,6'}$	6.3	C6	63.4	H6	3.94	$J_{5,6'}$	6.2	C6	63.5
H6′	≈3.82	$J_{6,6'}$	12.7			H6′	≈3.81	$J_{6,6'}$	12.5		
34[a]						**35**[a]					
H1	5.66	$J_{1,2}$	6.6	C1	101.1	H1	5.66	$J_{1,2}$	6.6	C1	101.1
H2	4.84	$J_{2,3}$	4.3	C2	75.8	H2	4.85	$J_{2,3}$	4.3	C2	75.8
H3	4.43	$J_{3,4}$	2.3	C3	74.1	H3	4.43	$J_{3,4}$	2.7	C3	74.1
H4	4.32	$J_{4,5}$	9.0	C4	84.4	H4	4.32	$J_{4,5}$	9.0	C4	84.4
H5	3.59	$J_{5,6}$	2.7	C5	71.4	H5	3.95	$J_{5,6}$	2.7	C5	71.5
H6	3.77	$J_{5,6'}$	5.1	C6	65.5	H6	3.77	$J_{5,6'}$	5.1	C6	65.5
H6′	3.68	$J_{6,6'}$	12.5			H6′	3.69	$J_{6,6'}$	12.1		

[a] D_2O; $T = 30\,°C$; internal ref. $Me_3Si(CH_2)_3SO_3Na$. [b] $CDCl_3$; $T = 20\,°C$; internal ref. TMS. [c] C_6D_6; $T = 20\,°C$; internal ref. TMS. [d] $CDCl_3/C_6D_6 = 2:1$; $T = 20\,°C$; internal ref. TMS.

to α-configurations of D-mannofuranoses.[84,85] For salt **35**, a small long-range coupling of approximately 0.3 Hz between H-1 and H-4 was observed. A similar long-range coupling has been reported for *N*-acetyl-α-L-rhamnofuranosylamine.[86] Acetylation of **35** with Ac_2O/pyridine at 5 °C afforded a pentaacetate, the ^1H and ^{13}C NMR spectra of which were identical to those reported for penta-*O*-acetyl-α-D-mannofuranose.[80]

Until now, the mechanistic reason for the different results of nitrosation of mannose oxime under acidic and basic conditions has not been clear. One probably has to apply the Curtin–Hammett principle to a protonated R−CH=N$^+$(NO)OH and a deprotonated R−CH=N$^+$(NO)O$^-$ transition state.[86] At present we are studying nitrosations of other carbohydrate oximes under basic conditions. Preliminary results show that these nitrosations proceed in a similar manner to that found for mannose oxime **30**.

Experimental Section

General: Solvents were dried by standard methods. All reactions were carried out with exclusion of moisture. Spectrometers used: ^1H (400.1 MHz) and ^{13}C (100.6 MHz) NMR spectra: JEOL JNM-LA-400 FT NMR system. Internal reference $SiMe_4$ (TMS) or $Me_3Si(CH_2)_3SO_3Na$ (PSIL); δ scale in ppm; coupling constants J in Hz. Signal assignments were supported by ^1H spin–spin decoupling and CH correlation experiments. IR spectra: Perkin–Elmer FTIR 1600 spectrometer; UV spectra: Perkin–Elmer Lambda 19 UV/Vis/near-IR spectrometer; solvent H_2O. Optical rotations: Perkin–Elmer 241 polarimeter.

Single-crystal X-ray analysis: Single-crystal X-ray diffraction analysis was performed with an Enraf–Nonius CAD4 four-circle diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) in the θ range of 2–26° with a scan width ω (°) of $0.5 + 0.35\tan\theta$ for both structures. The structures were solved by direct methods and refined by full-matrix, least-squares analyses with use of SHELX-97-2 software.[87] Non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were placed in calculated positions and refined isotropically.

CCDC-264902 (**14a**) and CCDC-264903 (**18**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal structure data for 14a: Formula $C_{35}H_{30}N_2O_{11}$ ($M_r = 654.61$); crystal dimensions $0.2 \times 0.2 \times 0.5$ mm; orthorhombic; space group $P2_12_12_1$; $a = 9.371(3)$, $b = 16.733(3)$, $c = 21.421(4)$ Å; $V = 3359(1)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.294$ g cm^{-3}; $2\theta_{max} = 24.079°$; $T = 183$ K; 6252 independent reflections ($R_{int} = 0.068$), of which 2817 were above $2\sigma(F^2)$; $R1 = 0.2457$; $wR2 = 0.1268$ with $I > 2\sigma(I)$; $R_\sigma = 0.0601$; GoF = 0.97; $\Delta\rho_{max} = 0.25$ e Å^{-3}; $\Delta\rho_{min} = -0.26$ e Å^{-3}.

Crystal structure data for 18: Formula $C_{15}H_{22}N_2O_{11}$ ($M_r = 406.4$); crystal dimensions $0.3 \times 0.3 \times 0.5$ mm; orthorhombic; space group $P2_12_12_1$; $a = 5.723(1)$, $b = 17.650(3)$, $c = 19.666(4)$ Å; $V = 1886.4(7)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.359$ g cm^{-3}; $2\theta_{max} = 31.575°$; $T = 153$ K; 3915 independent reflections ($R_{int} = 0.022$), of which 2762 were above $2\sigma(F^2)$; $R1 = 0.1065$; $wR = 0.1841$ with $I > 2\sigma(I)$; $R_\sigma = 0.0479$; GoF = 1.00; $\Delta\rho_{max} = 0.30$ e Å^{-3}; $\Delta\rho_{min} = -0.31$ e Å^{-3}.

***N*-Hydroxy-β-D-glucopyranosylamine (12)**: A suspension of $NH_2OH{\cdot}HCl$ (10.43 g, 150 mmol) in MeOH (100 mL) was stirred at 23 °C for 15 min. The resulting clear solution was cooled to 5 °C and Me_3COK (15.71 g, 140 mmol) was added in portions. After the mixture had been stirred at 23 °C for 30 min, KCl was filtered off and washed with MeOH (50 mL). D-Glucose (18.02 g, 100 mmol) was added to the filtrate. After the mixture had been stirred at 23 °C for 12 h the solvent was evaporated from the clear solution and the oily residue (essentially open-chain oxime) was stirred at 23 °C in MeOH (20 mL) for 80 h, after which a colorless crystalline powder of the pure title compound **12** (15.92 g, 82 %) was filtered off and washed with MeOH (5 mL) and with Et_2O. Evaporation of the mother liquor left an oil, which consisted of **12** and the *E* and *Z* forms (**10** and **11**) of D-glucose oxime (**10**/**11**/**12** 1:5:2, by ^1H NMR). Stirring of the oil in MeOH (7 mL) for 3 days afforded a second fraction of pure crystalline **12** (2.63 g, 14 %). M.p. 120–122 °C (decomp 147–149 °C) (ref. [37]: decomp. 143–145 °C); $[\alpha]_D^{25} = -7.73$ ($c = 1.1$, H_2O, 5 min after dissolution) (ref. [37]: $[\alpha]_D^{25} = -10.7$ ($c = 1.1$, H_2O, 2 min after dissolution)); ^1H NMR (D_2O, 25 °C): $\delta = 4.19$ (d, $J = 9.3$ Hz; H-1), 3.40 (t, $J = 9.3$ Hz; H-2), 3.34–3.54 (m; H-3–H-5), 3.72 (dd, $J = 5.7$, 12.3 Hz; H-6), 3.90 (dd, $J = 2.1$, 12.3 Hz; H-6′); ^{13}C NMR (D_2O, 20 °C): $\delta = 93.6$ (C-1), 79.8, 79.4, 72.2, 72.1 (C-2–C-5), 63.6 (C-6). After this had been allowed to stand at 25 °C for 5 h the spectrum showed a mixture of the oximes **10**, **11**, and the hydroxylamine **12** (integral ratio 0.9:0.4:1.0).

^1H NMR (D_2O, 20 °C): $\delta = 7.51$ (d, $J = 7.0$ Hz; (*E*)-H-1), 6.88 (d, $J = 6.5$ Hz; (*Z*)-H-1), 4.39 (t, $J = 7.0$ Hz; (*E*)-H-2), 5.00 (t, $J = 6.5$ Hz; (*Z*)-H-2), 3.95 (m; (*E*)-,(*Z*)-H-3); ^{13}C NMR (D_2O, 25 °C): $\delta = 154.5$, 154.1 ((*E*)-,(*Z*)-C-1).

Ammonium 2-(β-D-glucopyranosyl)diazene-1-olate-2-oxide (13): HCl (1 M, 120 mL) was added at 0 °C to a solution of **12** (19.52 g, 100 mmol) in H_2O (100 mL). A solution of $NaNO_2$ (7.25 g, 105 mmol) in H_2O (100 mL) was added dropwise at 0 °C with stirring over the course of 1 h. Addition of aqueous NH_3 (25 %, 12 mL) and evaporation of the solvent under reduced pressure afforded a pale yellow solid, which according to the ^1H NMR spectrum consisted of a mixture of **13** (76 %) and α- and β-D-glucopyranose (6 % and 15 %), together with trace amounts of (*E*)- and (*Z*)-D-glucoseoximes **10** and **11**, and of at least five other sugars (not identified). The product was dissolved in warm H_2O (60 mL) containing a few drops of concentrated aqueous NH_3. On addition of MeOH (160 mL) compound **13** started to crystallize. After 48 h at 5 °C, fine colorless prisms (15.64 g, 65 %) of title compound **13** were isolated by filtration and washed with small amounts of MeOH and Et_2O. Decomposition with gas evolution and blackening 193–198 °C; $[\alpha]_D^{25} = -17.9$ ($c = 1.0$, H_2O); ^1H NMR (D_2O, 20 °C): $\delta = 5.29$ (d, $J = 9.0$ Hz; H-1), ≈3.93 (m; H-2), ≈3.88 (m; H-6), 3.77 (dd, $J = 5.1$, 12.5 Hz; H-6′), 3.65 (m; H-3, H-5), 3.51 (t, $J = 9.4$ Hz; H-4); ^{13}C NMR (D_2O, 20 °C): $\delta = 96.5$ (C-1), 80.8 (C-5), 78.5 (C3), 72.1 (C-2), 71.6 (C-4), 63.2 (C-6); UV (H_2O): λ_{max} (ε) = 254 nm (9816 M^{-1} cm^{-1}); elemental analysis calcd for $C_6H_{15}N_3O_7$ (241.2): C 29.87, H 6.27, N 17.43; found: C 29.77, H 6.21, N 17.44.

(*Z*)-1-Methoxy-2-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)diazene-2-oxide (14a) and *N*-methoxy-*N*-nitroso-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosylamine (14b): A suspension of **13** (2.41 g, 10 mmol), $NaHCO_3$ (2.52 g, 30 mmol), and Me_2SO_4 (3.78 g, 30 mmol) in H_2O (10 mL) was stirred at 23 °C for 24 h. After evaporation of the solvent the semisolid residue was suspended in hot pyridine (30 mL). PhCOCl (11.25 g, 80 mmol) was added at 5 °C. After 24 h at 5 °C the suspension was diluted with H_2O. The mixture was repeatedly extracted with $CHCl_3$, and the combined organic extracts were washed with HCl (1 M), then with aqueous $NaHCO_3$, and finally with H_2O. Evaporation of the solvent afforded a yellow resin, which crystallized on scratching under Et_2O (40 mL). After 12 h at 5 °C a colorless crystalline powder (4.23 g, 65 %) was isolated by filtration. Recrystallization from boiling EtOH (340 mL) furnished colorless needles of **14a** (3.64 g, 56 %) suitable for X-ray diffraction analysis. M.p. 194–195 °C; $[\alpha]_D^{25} = +17.8$ ($c = 1.2$, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 3.98$ (OMe), 4.42 (m; H-5), 4.56 (dd, $^3J = 5.3$, $^2J = 12.3$ Hz; H-6), 4.68 (dd, $^3J = 3.0$, $^2J = 12.3$ Hz; H-6′), 5.73 (d, $^3J = 9.0$ Hz; H-1), 5.83 (t, $^3J = 9.8$ Hz; H-4), 6.06 (dd, $^3J = 9.5$, 9.8 Hz; H-3), 6.19 (dd, $^3J = 9.0$ Hz, 9.5 Hz; H-2), 7.26–8.02 (m, 20 H; phenyl); ^{13}C NMR ($CDCl_3$, 20 °C): $\delta = 95.1$ (C-1), 61.9 (OMe), 62.7 (C-6), 68.7 (C-4), 69.1 (C-2), 72.8 (C-3), 75.4 (C-5), 128.4–129.9 (*o*,*m*,*p*-C, aryl), 133.2, 133.5, 133.6, 133.7 (*i*C, aryl), 164.2, 165.0, 165.7, 166.1 (CO); IR (CCl_4): $\tilde{\nu} = 1741$ (vs), 1266 (vs), 1245 (s), 1101 (s), 1090 (vs), 1069 (vs), 1027 cm^{-1} (s); UV (MeCN): λ_{max} (ε) = 230 (5477.4), 199 nm (5433.6 M^{-1} cm^{-1}); elemental analysis calcd for $C_{35}H_{30}N_2O_{11}$ (654.61): C 64.21, H 4.62, N 4.28; found: C 64.20, H 4.70, N 4.34. Evaporation of the ethereal mother liquor of the first crystallization

of **14a** left a brown syrup consisting of small amounts of **14a** and of at least two other carbohydrates (^{1}H NMR). The main component **14b** was isolated by column chromatography (silica gel 60 (Fluka), eluent Et_2O/hexane 1:1) as a moderately stable and not completely pure and noncrystallized pale yellow powder. Elemental analysis calcd for $C_{35}H_{30}N_2O_{11}$ (654.61): C 64.21, H 4.62, N 4.28; found: C 64.62, H 4.87, N 4.02. The ^{1}H NMR spectrum ($CDCl_3$) of **14b** showed partial decomposition within 1 h into a mixture of three new compounds (not identified).

Compound 14b: ^{1}H NMR (C_6D_6): $\delta = 6.06$ (d, $^3J = 9.4$ Hz; H-1), 6.24 (t, $^3J = 9.4$ Hz; H-2), 6.12 (t, $^3J = 9.7$ Hz; H-3), 5.90 (t, $^3J = 9.7$ Hz; H-4), 3.60 (m; H-5), 4.58 (dd, $^3J = 2.9$, $^2J = 12.5$ Hz; H-6), 4.28 (dd, $^3J = 4.6$, $^2J = 12.5$ Hz; H-6′), 3.49 (OMe), 6.76–8.17 (m, 20H; Ph); ^{13}C NMR (C_6D_6, 20 °C): $\delta = 89.5$ (C-1), 75.0, 74.1 (C-5,3), 69.4, 68.4 (C-4,2), 65.1 (br, OMe), 62.7 (C-6), 127.9–133.5 (Ph), 164.8, 165.3, 165.9, 166.1 (C=O).

***N*-Methoxy-*N*-nitroso-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (18)**: D-Glucose (1.80 g, 10 mmol) and $MeONH_2$·HCl (1.00 g, 12 mmol) were dissolved in warm pyridine (15 mL). After the mixture had been kept at 23 °C for 24 h, the solvent was evaporated and the oily residue was dissolved in H_2O (20 mL). $NaHCO_3$ (1.05 g, 12.5 mmol) was added (CO_2 evolution). Evaporation of the solvent afforded a colorless syrup of the *O*-methyloximes **15** and **16** (ratio 1.0:0.2). ^{1}H NMR (D_2O): $\delta = 7.53$ (d, $^3J = 6.7$ Hz; (*Z*)-H-1), 6.88 (d, $^3J = 6.6$ Hz; (*E*)-H-1), 4.39 (t, $^3J = 6.7$ Hz; (*Z*)-H-2), 4.92 (t, $^3J = 6.6$ Hz; (*E*)-H-2), 3.85 (s; (*Z*)-OMe), 3.88 (s; (*E*)-OMe), 3.57–3.95 (m, 10H); ^{13}C NMR (D_2O): $\delta = 153.6$ ((*Z*)-C-1), 154.5 ((*E*)-C-1), 64.1–79.8 (12C).

The crude mixture of **15**+**16** was dissolved in H_2O (10 mL). HCl (1M, 12 mL) was added at 0–5 °C and a solution of $NaNO_2$ (0.76 g, 11 mmol) in H_2O (10 mL) was added dropwise over 30 min. After the mixture had been stirred at 23 °C for a further 10 min, aqueous NH_3 (25%, 3 mL) was added. Evaporation of the solvent afforded the crude *N*-methoxy-*N*-nitroso-β-D-glucopyranosylamine (**17**) contaminated with small amounts of α- and β-D-glucopyranose. The product was taken up in MeOH (10 mL) and THF (10 mL). After 24 h at 23 °C the suspension was filtered.

Evaporation of the filtrate afforded a syrup, which was dissolved in MeOH (10 mL). Evaporation of the solvent furnished **17** as a yellow amorphous solid (1.83 g, 77%) still containing about 2% of α- and β-D-glucopyranose and other impurities. ^{1}H NMR (D_2O): $\delta = 5.84$ (d, $^3J = 9.4$ Hz; H-1), 3.91–3.98 (m; H-2, H-6, OCH_3), 3.76 (dd, $^3J = 5.8$, $^2J = 12.5$ Hz; H-6′), 3.65–3.72 (m; H-3, H-5), 3.51 (dd, $^3J = 9.4$, 9.7 Hz; H-4); ^{13}C NMR (D_2O): $\delta = 94.1$ (C-1), 81.1 (C-5), 78.74 (C-3), 71.72 (C-2), 71.6 (C-4), 67.9 (OMe), 63.2 (C-6).

The crude **17** was taken up in pyridine (10 mL) and Ac_2O (5 mL). After 12 h at 5 °C and a further 12 h at 23 °C the solvent was evaporated. The oily residue was repeatedly extracted with $CHCl_3$/HCl (1M)/H_2O. Evaporation of the combined organic extracts afforded a yellow oil, which was crystallized at −15 °C from THF/pentane (7:10 mL) to furnish the title compound **18** as a yellow crystalline powder (2.62 g, 65%). Recrystallization at 50 °C from EtOH (1 g from 20 mL EtOH) afforded prisms suitable for X-ray diffraction analysis. M.p. 132–134 °C; dissolved in $CDCl_3$, compound **18** decomposed within a few days; $[\alpha]_D^{25} = +33.0$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 6.02$ (d, $^3J = 9.4$ Hz; H-1), 5.50 (t, $^3J = 9.4$ Hz; H-2), 5.38 (t, $^3J = 9.4$ Hz; H-3), 5.21 (t, $^3J = 9.7$ Hz; H-4), 4.28 (dd, $^3J = 4.9$, $^2J = 12.5$ Hz; H-6), 4.22 (dd, $^3J = 2.0$, $^2J = 12.5$ Hz; H-6′), 3.96 (m; H-5), 3.86 (OMe), 2.10, 2.07, 2.03, 1.96 ($OCCH_3$); ^{13}C NMR ($CDCl_3$): $\delta = 170.6$, 170.2, 169.3, 168.8 (C=O), 89.0 (C-1), 74.5 (C-5), 73.2 (C-3), 67.6 (C-4), 67.3 (C-2), 65.5 (OMe), 61.6 (C-6); UV (MeCN): λ_{max} (ε) = 233 nm (5500 $M^{-1}cm^{-1}$); elemental analysis calcd for $C_{15}H_{22}N_2O_7$ (406.4): C 44.33, H 5.46, N 6.90; found: C 44.32, H 5.35, N 6.80.

(*Z*)-1-Methoxy-2-(2,3,4,6-tetra-*O*-acetyl-1-deoxy-β-D-glucopyranosyl)diazene-2-oxide (19): Me_2SO_4 (3.78 g, 30 mmol) was added to a suspension of **13** (2.41 g, 10 mmol) and $NaHCO_3$ (2.52 g, 30 mmol) in H_2O (10 mL). After the mixture had been stirred at 23 °C for 48 h the solvent was evaporated under reduced pressure. The resulting yellow syrup was taken up in hot pyridine (30 mL). The suspension was cooled to 5 °C and Ac_2O (10 mL) was added. After the mixture had been stirred at 23 °C for 24 h the solvent was evaporated and the solid residue was dissolved in $CHCl_3$ and HCl (1M). The mixture was repeatedly extracted with $CHCl_3$ and the combined organic extracts were washed with H_2O and dried over Na_2SO_4. Evaporation of the solvent left a yellow crystalline residue (4.04 g, 99%) consisting of **19** and of the isomer **18** (ratio 1.00:0.23; ^{1}H NMR). Recrystallization from boiling EtOH (40 mL) afforded (at 5 °C) pale yellow needles (3.13 g, 77%; **19**/**18** = 1.00:0.10). Another crystallization from EtOH furnished colorless needles of the pure title compound **19**. Compounds **18** and **19** were also separated by column chromatography (silica gel 60, Fluka; eluent hexane/$CHCl_3$ 1:1).

Compound 19: M.p. 148–149 °C; $[\alpha]_D^{25} = -24.1$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 2.00$, 2.03, 2.05, 2.10 (acetyl), 3.92 (m; H-5), 4.12 (OMe), 4.19 (dd, $^3J = 2.3$, $^2J = 12.6$ Hz; H-6), 4.28 (dd, $^3J = 4.9$, $^2J = 12.6$ Hz; H-6′), 5.23 (t, $^3J = 9.5$ Hz; H-4), 5.35 (d, $^3J = 9.2$ Hz; H-1), 5.33 (t, $^3J = 9.5$ Hz; H-3), 5.65 (t, $^3J = 9.4$ Hz; H-2); ^{13}C NMR ($CDCl_3$): $\delta = 20.4$, 20.5, 20.5, 20.7 (acetyl-Me), 61.5 (C-6), 62.0 (OMe), 67.2 (C-4), 68.4 (C-2), 72.7 (C-3), 75.0 (C-5), 94.7 (C-1), 168.4, 169.2, 170.2, 170.6 (C=O); IR (CCl_4): $\tilde{\nu} = 1752$ (vs), 1506 (s), 1438 (m), 1368 (s), 1236 (vs), 1208 (vs), 1061 (vs), 1035 (s), 1020 cm^{-1} (s); UV (MeCN): λ_{max} (ε) = 239 nm (7520 $M^{-1}cm^{-1}$); elemental analysis calcd for $C_{15}H_{22}N_2O_{11}$ (406.35): C 44.33, H 5.46, N 6.90; found: C 44.41, H 5.40, N 6.87.

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-2-phenyldiazene-2-oxide (20): A solution of cupferron (1.56 g, 10 mmol) in DMSO (10 mL) was cooled to 5 °C. After addition of α-acetobromoglucose (2.06 g, 5 mmol) the mixture soon solidified. After the system had been allowed to warm to 23 °C over 5 h and stirred at 23 °C for 24 h, H_2O (50 mL) was added to the orange-brown solution. Extraction with Et_2O (3×50 mL), drying of the extracts over Na_2SO_4, and evaporation of the solvent under reduced pressure afforded a dark red syrup, which was dissolved in Et_2O (20 mL). After 24 h at −15 °C, compound **20** (0.94 g, 40%) was isolated by filtration as a brownish crystalline powder. Evaporation of the filtrate afforded a brown oil, which according to its NMR spectra consisted of **20**, azoxybenzene, and α- and β-2,3,4,6-tetra-*O*-acetyl-D-glucopyranose.[88] The crude **20** was dissolved in boiling ethyl acetate (4 mL). After addition of hexane (4 mL) and keeping at 5 °C for 3 days, almost colorless prisms (0.70 g) of title compound **20** were filtered off. M.p. 148–150 °C; $[\alpha]_D^{23} = +27.3$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR ($CDCl_3$/[D_6]benzene = 2:1): $\delta =$ 7.89 (d, $^3J = 7.4$ Hz; 2H; phenyl), 7.22–7.32 (m, 3H; phenyl), 5.54 (dd, $^3J = 9.4$, 8.2 Hz; H-2), 5.35 (d, $^3J = 8.2$ Hz; H-1), 5.32 (t, $^3J = 9.4$ Hz; H-3), 5.20 (dd, $^3J = 9.8$, 9.4 Hz; H-4), 4.23 (dd, $^3J = 4.7$, $^2J = 12.5$ Hz; H-6), 4.08 (dd, $^3J = 2.3$, $^2J = 12.5$ Hz; H-6′), 3.66 (m; H-5); ^{13}C NMR ($CDCl_3$/[D_6]benzene = 2:1): $\delta = 170.4$, 170.1, 169.2, 169.0 (C=O), 143.4, 131.7, 129.0, 121.5 (phenyl), 100.9 (C-1), 72.9, 72.8 (C-3,5), 69.4 (C-2), 67.8 (C-4), 61.5 (C-6), 20.4–20.5 (4×CH_3); IR (CCl_4): $\tilde{\nu} = 1762$ (vs), 1487 (s), 1441 (m), 1367 (s), 1315 (w), 1244 (vs), 1226 (vs), 1212 (vs, shoulder), 1152 (w), 1113 (m, shoulder), 1082 (vs), 1055 (s), 1037 (vs), 1013 cm^{-1} (s); UV (H_2O): λ_{max} (ε) = 254 (10310), 198 nm (13647 $M^{-1}cm^{-1}$); elemental analysis calcd for $C_{20}H_{24}N_2O_{11}$ (468.41): C 51.28, H 5.17, N 5.98; found: C 51.17, H 5.21, N 6.12.

D-Xylose oximes 21: These compounds were prepared from D-xylose (15.01 g, 100 mmol) in the manner described for **12**. After evaporation of MeOH and drying at 80 °C/10^{-1} torr for 20 h, **21** was obtained as a pale yellow syrup (16.35 g, 99%). $[\alpha]_D^{25} = -0.3$ ($c = 1.2$, H_2O; no change over 5 months); ^{1}H NMR (D_2O, 25 °C): $\delta = 7.54$ (d, $^3J = 6.3$ Hz; (*E*)-H-1, integral 1.00), 6.90 (d, $^3J = 6.3$ Hz; (*Z*)-H-1, integral 0.22), 4.12 (d, $^3J = 9.0$ Hz; H-1 of *N*-hydroxy-β-D-xylopyranosylamine, integral 0.03), 4.38 (dd, $^3J = 6.3$, 5.8 Hz; (*E*)-H-2), 4.97 (dd, $^3J = 6.3$, 4.9 Hz; (*Z*)-H-2), 3.61–3.80 (m; (*E*)-,(*Z*)-H-3,4,5,5′); ^{13}C NMR (D_2O, 25 °C): $\delta = 154.3$ ((*E*)-C-1), 155.0 ((*Z*)-C-1), 72.4 ((*E*)-C-2), 68.0 ((*Z*)-C-2), 74.7 ((*E*)-C-3), 74.2 ((*Z*)-C-3), 73.7 ((*E*)-C-4), 74.1 ((*Z*)-C-4), 65.3 ((*E*)-C-5), 65.2 ((*Z*)-C-5).

Ammonium 2-(β-D-xylopyranosyl)diazene-1-olate-2-oxide (22): The mixture of compounds **21** (1.65 g, 10 mmol) was dissolved in H_2O (20 mL), and HCl (1M, 14 mL) was added at 0 °C. A solution of $NaNO_2$ (0.83 g, 12 mmol) in H_2O (30 mL) was added dropwise with stirring over the course of 30 min. After the mixture had been stirred for a further 10 min, aqueous NH_3 (25%, 1 mL) was added. Evaporation of the solvent under reduced pressure furnished a pale yellow solid (2.73 g). The ^{1}H NMR spectrum of the crude product showed a mixture of **22** (≈79%), α- and β-D-xylopyranose (≈8% each), and trace amounts of at least four other sugars (not identified) but no starting material **21**. The product was dissolved in warm H_2O (10 mL). On addition of MeOH (20 mL) compound

22 started to crystallize. After 48 h at 5 °C the pure title compound **22** (1.08 g, 51 %) was filtered off as a colorless crystalline powder. Decomp. (blackening) above 80 °C; $[\alpha]_D^{25} = -55.6$ ($c = 1.0$, H_2O); ^{1}H NMR (D_2O): $\delta = 5.22$ (d, $^3J = 9.0$ Hz; H-1), 3.92 (t, $^3J = 9.1$ Hz; H-2), 3.59 (t, $^3J = 9.3$ Hz; H-3), 3.72 (m; H-4), 3.47 (t, ^2J,$^3J \approx 10.9$ Hz; H-5a), 4.07 (dd, $^3J = 5.5$, $^2J = 11.3$ Hz; H-5e); ^{13}C NMR (D_2O): $\delta = 97.2$ (C1), 78.7 (C3), 72.0 (C2), 71.4 (C4), 70.1 (C5); UV (H_2O): λ_{max} (ε) = 254 nm (4788 M^{-1} cm^{-1}); elemental analysis calcd for $C_5H_{13}N_3O_6$ (211.2): C 28.44, H 6.21, N 19.90; found: C 28.38, H 5.97, N 19.41. Compound **22** turned brown in the course of a few months at 23 °C.

***N*-Methoxy-*N*-nitroso-2,3,4-tri-*O*-acetyl-β-D-xylopyranosylamine (25)**: This compound was prepared from D-xylose (1.51 g, 10 mmol) and $MeONH_2$·HCl (1.00 g, 12 mmol) in the manner described for **18**. The D-xylose *O*-methyloxime **23**[52–54] was obtained as a moderately stable pale yellow syrup (ratio *Z*/*E* forms 1.0:0.2). ^{1}H NMR (D_2O): $\delta = 7.55$ (d, $^3J = 6.3$ Hz; (*Z*)-H-1), 6.91 (d, $^3J = 6.2$ Hz; (*E*)-H-1), 4.89 (t, $^3J = 5.5$ Hz; (*E*)-H-2), 4.38 (t, $^3J = 5.8$ Hz; (*Z*)-H-2), 3.88 ((*E*)-OMe), 3.86 ((*Z*)-OMe), 3.59–3.84 (m, 8H; (*E*)-,(*Z*)-H-3 to H-5); ^{13}C NMR (D_2O): $\delta = 154.9$ ((*E*)-C-1), 153.9 ((*Z*)-C-1), 74.6, 73.6, 72.2, 65.2, 64.0 ((*Z*)-C-2 to C-5, (*Z*)-OMe), 74.1, 73.9, 68.3, 65.1, 64.4 ((*E*)-C-2 to C-5, (*E*)-OMe). The *N*-methoxy-*N*-nitroso-β-D-xylopyranosylamine (**24**) was obtained as a brownish solid contaminated with small amounts of α- and β-D-xylose (ca. 8 %), **23** (ca. 2 %), and other impurities (ca. 4 %). ^{1}H NMR (D_2O): $\delta = 5.78$ (d, $^3J = 9.3$ Hz; H-1), 3.93 (t, $^3J \approx 9.3$ Hz; H-2), 3.64 (t, $^3J = 9.2$ Hz; H-3), 3.72 (m; H-4), 3.53 (t, $^{2,3}J \approx 11$ Hz; H-5a), 4.10 (dd, $^3J = 5.3$, $^2J = 11.3$ Hz; H-5e), 3.99 (OMe); ^{13}C NMR (D_2O): $\delta = 94.7$ (C-1), 78.9 (C-3), 71.7 (C-2), 71.3 (C-4), 70.2 (C-5), 67.9 (OMe). Acetylation of **24** afforded a pale yellow solid, which was crystallized from hot EtOH (25 mL) to give pale yellow needles (2.06 g, 62 %) of title compound **25**. Another crystallization from EtOH furnished long, pale yellow needles. M.p. 123–125 °C; $[\alpha]_D^{23} = -1.7$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 5.92$ (d, $^3J = 9.0$ Hz; H-1), 5.44 (t, $^3J \approx 9.1$ Hz; H-2), 5.37 (t, $^3J \approx 9.3$ Hz; H-3), 5.10 (m, $^3J \approx 5.5$, ≈ 10.5 Hz; H-4), 4.28 (dd, $^3J = 5.5$, $^2J = 11.5$ Hz; H-5e), 3.86 (OCH_3), 3.52 (dd, $^3J \approx 10.5$, $^2J = 11.5$ Hz; H-5a), 2.08, 2.06, 1.96 (CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 89.6$ (C-1), 67.4 (C-2), 72.8 (C-3), 68.5 (C-4), 65.1 (C-5), 65.5 (OMe), 168.9, 169.8, 170.2 (C=O), 20.4, 20.6, 20.7 (CH_3); IR (CCl_4): $\tilde{\nu}$ = 1764 (vs), 1505 (m), 1424 (m), 1369 (s), 1241 (vs), 1217 (vs), 1121 (m), 1087 (m), 1035 cm^{-1} (s); UV (MeCN): λ_{max} (ε) = 234 nm (5000 M^{-1} cm^{-1}); elemental analysis calcd for $C_{12}H_{18}N_2O_9$ (334.3): C 43.11, H 5.43, N 8.38; found: C 43.16, H 5.42, N 8.21.

D-Lactose oximes 26 and 27:[60] These compounds were prepared from D-lactose·H_2O (36.03 g, 100 mmol), NH_2OH·HCl (17.38 g, 250 mmol) and Me_3COK (26.93 g, 240 mmol) in MeOH (170 mL) in the manner described for compound **12**, except that the reaction mixture was stirred at 23 °C for 8 days. Filtration afforded the oxime (35.73 g, 98 %) contaminated with ≈2 % of D-lactose. The product was dissolved in hot H_2O (70 mL). After filtration and addition of hot EtOH (350 mL) the mixture was kept at 5 °C for 3 days. Filtration afforded a crystalline mixture (23.23 g, 65 %) of the *E*- and *Z*-oximes **26** and the hydroxylamine **27**. M.p. 183–185 °C (decomp.) (ref. [60]: m.p. 183–185 °C); $[\alpha]_D^{23}$ ($c = 1.0$, H_2O) = +27.8 (at 23 °C 10 min after dissolution) to +10.2 (at 23 °C 10 days after dissolution) (ref. [60]: $[\alpha]_D^{22}$ ($c = 1$, H_2O) = +38.3 (5 min after dissolution) to +15.5 (25 h after dissolution)); ^{1}H NMR (D_2O, 30 °C) (10 min after dissolution: (*E*)-**26**/(*Z*)-**26**/**27** ≈ 0.3:1.0:0.01); 26 days after dissolution: (*E*)-**26**/(*Z*)-**26**/**27** ≈ 5.3:1.0:2.3: $\delta = 7.61$ (d, $^3J = 5.9$ Hz; (*E*)-H-1), 6.95 (d, $^3J = 5.9$ Hz; (*Z*)-H-1), 5.03 (dd, $^3J = 5.8$, 4.7 Hz; (*Z*)-H-2), 4.56 (dd, $^3J = 6.6$, 5.9 Hz; (*E*)-H-2), 4.52 (d, $^3J = 7.9$ Hz; (*Z*)-H-1′), 4.49 (d, $^3J = 7.8$ Hz; (*E*)-H-1′), 4.45 (d, $^3J = 7.8$ Hz; **27**: H-1′), 4.22 (d, $^3J = 9.0$ Hz; **27**: H-1), 4.07 (dd, $^3J = 2.7$, 4.7 Hz; (*Z*)-H-3), 3.52–3.98 (m; other H atoms of the *E* and *Z* form, and of **27**), 3.45 (dd, $^3J = 9.4$, 9.0 Hz; **27**: H-2); ^{13}C NMR (D_2O, 30 °C): $\delta = 154.8$, 154.6 ((*E*)-,(*Z*)-C-1), 106.0, 105.6 ((*E*)-,(*Z*)-C-1′), 93.5 (**27**: C-1), 82.5, 81.0, 80.7, 78.7, 78.1, 78.0, 77.9, 77.8, 75.3, 74.0, 73.9, 73.8, 73.7, 73.6, 73.0, 72.1, 71.8, 71.3, 71.2, 68.5, 64.8, 64.7, 63.8, 63.7, 63.4, 62.9.

Diphenylmethylammonium 4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosyldiazene-1-olate-2-oxide (28): HCl (1 M, 3 mL) was added to a cooled (0–5 °C) suspension of **26**+**27** (1.08 g, 3 mmol) in H_2O (3 mL). A solution of $NaNO_2$ (0.21 g, 3 mmol) in H_2O (5 mL) was added dropwise with stirring over the course of 20 min. Benzhydrylamine (0.55 g, 3 mmol) was added to the acidic clear solution. Evaporation under reduced pressure afforded a colorless solid (1.98 g), which was dissolved in hot H_2O (20 mL) and EtOH (20 mL). Crystallization at 5 °C afforded colorless, fine needles (1.28 g, 75 %). To remove traces of EtOH the product was suspended in H_2O (10 mL). Evaporation under reduced pressure furnished the pure title compound **28.** Decomposition with gas evolution and blackening 180–200 °C; $[\alpha]_D^{23} = +6.9$ ($c = 1.0$, H_2O); ^{1}H NMR (D_2O, 30 °C): $\delta = 7.42$–7.52 (m, 10H; phenyl), 5.72 (s; NCH), 5.32 (d, $^3J = 9.0$ Hz; H-1), 4.49 (d, $^3J = 7.8$ Hz; H-1′), 4.01–3.73 (m, 10H; H-2 (3.99), H-4′ (3.94), H-3 (3.79), H-4,5,5′,6,6′,6″,6‴), 3.67 (dd, $^3J = 3.5$, 9.8 Hz; H-3′), 3.57 (dd, $^3J = 7.8$, 9.8 Hz; H-2′); ^{13}C NMR (D_2O, 30 °C): $\delta = 139.4$, 132.0, 131.7, 129.8 (phenyl), 105.6 (C-1′), 96.4 (C-1), 80.1 (C-5), 79.7 (C-5′), 78.1 (C-3), 77.2 (C-4′), 75.3 (C-3′), 73.7 (C-2′), 71.8 (C-2), 71.3 (C-4), 63.7, 62.6 (C-6,6′), 60.6 (NCH); UV (H_2O): λ_{max} (ε) = 256 (9100), 198 nm (25000 M^{-1} cm^{-1}); elemental analysis calcd for $C_{25}H_{35}N_3O_{12}$ (569.6): C 52.72, H 6.19, N 7.38; found: C 52.82, H 5.82, N 7.32.

D-Fructose oxime (29):[73–75] This compound was prepared from D-fructose (18.02 g, 100 mmol) in the manner described for the preparation of **12**. The crude oily product consisted of a mixture of the *Z* and *E* forms of **29** (ratio 1.0:0.9; ^{1}H NMR). Crystallization from MeOH (30 mL) afforded a colorless powder of the pure *Z* isomer **29** (18.36 g, 94 %). In aqueous solution slow *Z*⇔*E* equilibration took place. After 5 days at 23 °C an equilibrium *Z*/*E* ≈ 1:1 was reached. ^{1}H NMR (D_2O, 25 °C): $\delta = 5.28$ (d, $^3J = 2.3$ Hz; (*Z*)-H-3), 4.32 (s, 2H; (*Z*)-H-1), 3.92 (dd, $^3J = 2.2$, 8.4 Hz; (*Z*)-H-4), 3.83 (dd, $^3J = 2.7$, $^2J = 11.7$ Hz; (*Z*)-H-6), 3.77 (m; (*Z*)-H-5), 3.64 (dd, $^3J = 6.2$, $^2J = 11.7$ Hz; (*Z*)-H-6′), 4.67 (d, $^3J = 2.8$ Hz; (*E*)-H-3), 4.52 (d, $^2J = 14.8$ Hz; (*E*)-H-1), 4,37 (d, $^3J = 14.8$ Hz; (*E*)-H-1′), ≈3.76–3.85 (m; (*E*)-H-4,5,6), ≈3.65 (m; (*E*)-H-6′); ^{13}C NMR (D_2O; 25 °C): $\delta = 164.1$ ((*Z*)-C-2), 162.8 ((*E*)-C-2), 74.4 ((*E*)-C-4), 74.1 ((*Z*)-C-4), 73.7 ((*E*)-C-5), 73.6 ((*Z*)-C-5), 72.5 ((*E*)-C-3), 69.1 ((*Z*)-C-3), 65.7, 65.6 ((*Z*,*E*)-C-6), 62.7 ((*Z*)-C-1), 57.5 ((*E*)-C-1). Nitrosation of the oxime **29** in the manner described for **12** exclusively furnished D-fructose.

D-Mannose oxime (30):[37,76–78] This compound was prepared from D-mannose (18.02 g, 100 mmol), NH_2OH·HCl (10.43 g, 150 mmol), and Me_3COK (15.71 g, 140 mmol) in the manner described for the preparation of **12**, except that after addition of D-mannose the mixture was stirred at 5 °C for 3 days. Filtration and washing of the residue with MeOH and Et_2O afforded colorless crystals (19.40 g, 100 %), which were dissolved in hot H_2O (100 mL). Addition of MeOH (100 mL) and keeping at 5 °C for 48 h furnished colorless prisms of title compound **30** (16.90 g, 87 %, *E*/*Z* = 1.0:0.1).[77] M.p. 183–185 °C (decomp.) (ref. [37]: m.p. 184 °C; ref. [77]: m.p. 188–183 °C). $[\alpha]_D^{23} = +6.3$ ($c = 1.0$, H_2O, 5 min after dissolution) (ref. [37]: $[\alpha]_D^{25} = +7.0$ ($c = 1.0$, H_2O, 3 min after dissolution)); ^{1}H NMR (D_2O, 30 °C): $\delta = 7.58$ (d, $^3J = 7.0$ Hz; (*E*)-H-1), 6.97 (d, $^3J = 6.7$ Hz; (*Z*)-H-1), 4.97 (dd, $^3J = 6.7$, 7.4 Hz; (*Z*)-H-2), 4.28 (dd, $^3J = 7.0$, 8.2 Hz; (*E*)-H-2), 3.95 (m; (*Z*)-H-3), 3.93 (dd, $^3J = 8.2$, 1.1 Hz; (*E*)-H-3), 3.85 (dd, $^3J = 2.3$, $^2J = 11.7$ Hz; (*E*)-H-6), 3.77 (m; (*E*)-H-4, (*E*)-H-5), 3.67 (m; (*E*)-H-6′); ^{13}C NMR (D_2O, 30 °C): $\delta = 155.4$ (m; (*E*)-C-1), 155.0 (m; (*Z*)-C-1), 73.5 ((*E*)-C-4), 73.2 ((*E*)-C-3), 72.2 ((*Z*)-C-3), 71.8 ((*E*)-C-5), 71.4 ((*E*)-C-2), 66.1 ((*Z*)-C-6), 65.8 ((*E*)-C-6).

1-Hydroxy-2-(β-D-mannopyranosyl)diazene-2-oxide (32): Slow (45 min) addition of a solution of $NaNO_2$ (0.70 g, 10 mmol) in H_2O (10 mL) to a cooled (0–3 °C) stirred suspension of **30** (1.95 g, 10 mmol) in HCl (0.5 M, 20 mL) afforded an acidic clear solution, which was quickly neutralized by addition of *p*-anisidine (1.23 g, 10 mmol, crushed powder). After the mixture had been stirred at 23 °C for 30 min the solvent was evaporated under reduced pressure. The brownish amorphous residue essentially consisted of the *p*-anisidinium salt **31**. ^{1}H NMR (D_2O, 30 °C): $\delta = 5.42$ (d, $^3J = 0.8$ Hz; H-1), 4.44 (dd, $^3J = 0.8$, 1.9 Hz; H-2), 3.96 (dd, $^3J = 2.4$, $^2J = 12.5$ Hz; H-6), 3.72–3.86 (m; H-3,4,6′), 3.59 (m; H-5), 7.05 (d, $J = 9.2$, 2H), 7.25 (d, $J = 9.2$ Hz; 2H; aryl); ^{13}C NMR (D_2O, 30 °C): $\delta = 160.4$, 129.3, 125.5, 118.0 (aryl), 94.7 (C-1), 72.3 (C-2), 75.5 (C-3), 69.0 (C-4), 81.9 (C-5), 63.5 (C-6), 58.4 (OCH_3).

The crude product was suspended in MeOH (55 mL). After 5 min of ultrasonic irradiation at 20 °C, THF (40 mL) was added. The mixture was kept at 5 °C for 48 h. Filtration afforded a colorless powder (1.42 g). In order to remove NaCl the crude product was suspended in H_2O (10 mL).

After 5 min of ultrasonic irradiation at 20 °C the suspension was kept at 5 °C for 24 h. Filtration furnished title compound **32** as a colorless powder (1.11 g, 50 %). Decomposition with gas evolution 170–180 °C; $[\alpha]_D^{23} = +52.7$ ($c = 1.0$, H_2O); ^{1}H NMR (D_2O, 30 °C): $\delta = 5.58$ (d, $^3J =$ 1.2 Hz; H-1), 4.47 (dd, $^3J = 1.2$, 3.1 Hz; H-2), 3.97 (dd, $^3J = 2.3$, $^2J =$ 12.7 Hz; H-6), ≈3.81 (m; H-3, H-6′), 3.69 (dd, $^3J = 9.7$, 9.8 Hz; H-4), ≈3.60 (ddd, $^3J = 2.3$, 6.3, 9.8 Hz; H-5); ^{13}C NMR (D_2O, 30 °C): $\delta = 97.4$ (C-1), 72.0 (C-2), 75.2 (C-3), 68.8 (C-4), 82.1 (C-5), 63.4 (C-6); UV (H_2O): λ_{max} (ε) = 230 nm (5417 $M^{-1}cm^{-1}$); elemental analysis calcd for $C_6H_{12}N_2O_7$ (224.2): C 32.14, H 5.40, N 12.50; found: C 32.08, H 5.34, N 12.36.

Sodium 2-(β-D-mannopyranosyl)diazene-1-olate-2-oxide (33): Compound **32** (1.12 g, 5 mmol) was added to a cold (0–5 °C) solution of $NaHCO_3$ (0.42 g, 5 mmol) in H_2O (10 mL). After 5 min of ultrasonic irradiation the almost clear solution was filtered. On addition of MeOH (20 mL) and THF (20 mL) the filtrate became turbid. After 2 months at 0–5 °C colorless prisms of title compound **33** (0.77 g, 63 %) were isolated by filtration. Decomposition with gas evolution 222–230 °C; $[\alpha]_D^{25} = +23.2$ ($c =$ 1.0, H_2O); ^{1}H NMR (D_2O, 30 °C): $\delta = 5.37$ (d, $^3J \approx 0.1$ Hz; H-1), 4.43 (dd, $^3J \approx 0.1$, 2.3 Hz; H-2), ≈3.77 (H-3), 3.74 (t, $^3J \approx 9.4$ Hz; H-4), 3.58 (ddd, ^3J ≈2.3, 6.2, 9.0 Hz; H-5), 3.94 (dd, $^3J \approx 2.3$, $^2J \approx 12.5$ Hz; H-6), ≈3.81 (H-6′); ^{13}C NMR (D_2O, 30 °C): $\delta = 93.9$ (C-1), 72.3 (C-2), 75.6 (C-3), 69.0 (C-4), 81.8 (C-5), 63.5 (C-6); UV (H_2O): λ_{max} (ε) = 253 nm (7970 $M^{-1}cm^{-1}$); elemental analysis calcd for $C_6H_{11}N_2NaO_7$ (246.2): C 29.27, H 4.50, N 11.38; found: C 29.18, H 4.65, N 11.10.

Cesium 2-(α-D-mannofuranosyl)diazene-1-olate-2-oxide (34): Isopentyl nitrite (3.52 g, 30 mmol), and then a solution of $CsOH \cdot H_2O$ (1.85 g, 11 mmol) in H_2O (5 mL), were added at 5 °C to a suspension of compound **30** (1.96 g, 10 mmol) in MeOH (20 mL). Stirring at 5 °C for 24 h, filtration and washing of the residue with MeOH and Et_2O furnished a colorless powder (3.00 g, 84 %), which was dissolved in H_2O (30 mL). After addition of MeOH (300 mL) and keeping at 5 °C for 3 days, colorless fine needles of title compound **34** (2.10 g, 59 %) were isolated by filtration and washed with MeOH and Et_2O. Decomposition with evolution of gas and blackening 198–203 °C; $[\alpha]_D^{23} = +79.0$ ($c = 1.0$, H_2O); ^{1}H NMR (D_2O, 30 °C): $\delta = 5.66$ (d, $^3J = 6.6$ Hz; H-1), 4.84 (dd, $^3J = 6.6$, 4.3 Hz; H-2), 4.43 (dd, $^3J = 4.3$, 2.3 Hz; H-3), 4.32 (dd, $^3J = 2.3$, $^2J = 9.0$ Hz; H-4), 3.95 (m; H-5), 3.77 (dd, $^3J = 2.7$, $^2J = 12.5$ Hz; H-6), 3.68 (dd, $^3J = 5.1$, $^2J =$ 12.5 Hz; H-6′); ^{13}C NMR (D_2O): $\delta = 101.1$ (C-1), 75.8 (C-2), 74.1 (C-3), 84.4 (C-4), 71.4 (C-5), 65.5 (C-6); UV (H_2O): λ_{max} (ε) = 253 nm (9337 $M^{-1}cm^{-1}$); elemental analysis calcd for $C_6CsH_{11}N_2O_7$ (356.1): C 20.24, H 3.11, N 7.87; found: C 20.37, H 3.13, N 7.75.

Potassium 2-(α-D-mannofuranosyl)diazene-1-olate-2-oxide (35): With KOH (0.62 g, 11 mmol) in place of $CsOH \cdot H_2O$ the procedure for the preparation of **34** afforded the K salt **35** as a crystalline colorless powder (2.31 g, 88 %). Decomposition with evolution of gas and blackening 212–215 °C; $[\alpha]_D^{23} = +108.1$ ($c = 1.0$, H_2O); ^{1}H NMR (D_2O): $\delta = 5.66$ (dd, $^3J =$ 6.6, $^4J \approx 0.3$ Hz; H-1), 4.85 (dd, $^3J = 6.6$, 4.3 Hz; H-2), 4.43 (dd, $^3J = 4.3$, 2.7 Hz; H-3), 4.32 (ddd, $^4J \approx 0.3$, $^3J = 2.7$, 9.0 Hz; H-4), 3.95 (m; H-5), 3.77 (dd, $^3J = 2.7$, $^2J = 12.1$ Hz; H-6), 3.69 (dd, $^3J = 5.1$, $^2J = 12.1$ Hz; H-6′); ^{13}C NMR (D_2O): $\delta = 101.1$ (C-1), 75.8 (C-2), 74.1 (C-3), 84.4 (C-4), 71.5 (C-5), 65.5 (C-6); UV (H_2O): λ_{max} (ε) = 253 nm (9237 $M^{-1}cm^{-1}$); elemental analysis calcd for $C_6H_{11}KN_2O_7$ (262.3): C 27.48, H 4.23, N 10.68; found: C 27.52, H 4.28, N 10.45. Acetylation of **35** with Ac_2O/pyridine at 5 °C afforded a pentaacetate, the ^{1}H and ^{13}C NMR spectra of which were identical to those reported for penta-*O*-acetyl-α-D-mannofuranose.[80]

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