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E versus *Z* geometry in β-D-*arabino*-hexopyranosidulose oximes ☆

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ABSTRACT

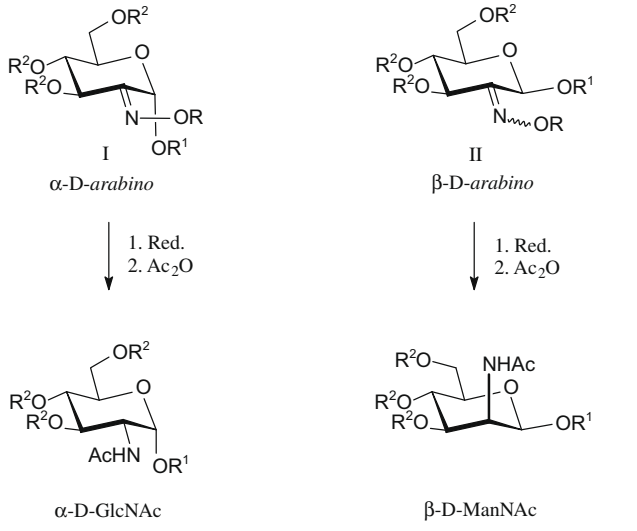
Koenigs–Knorr-type glycosidations of peracylated 2*Z*-benzoyloxyimino-glycopyranosyl bromides invariably proceed with retention of the *Z*-geometry. Accordingly, the many β-D-hexosidulose oximes in literature which were prepared in this way and for which the oxime geometry has not been addressed explicitly, are the *Z*-oximes throughout. By contrast, oximation of β-D-hexopyranosid-2-uloses leads to mixtures of *E* and *Z* oximes readily separable and structurally verifiable by ^{1}H and ^{13}C NMR. Configurational assignments rested on comparative evaluation of NMR data of *E* and *Z* isomers, and, most notably on an X-ray structural analysis of the pivaloylated isopropyl 2*E*-benzoyloxyimino-2-deoxy-β-D-*arabino*-hexopyranoside revealing the unusual $^{1}S_{5} \rightleftharpoons {}^{1,4}B$ conformation for the pyranoid ring.

1. Introduction

Within the last two decades, oximes of D-*arabino*-hexopyranosiduloses have figured prominently as key intermediates for the straightforward preparation—by reduction and N-acetylation—of oligosaccharides with α-D-GlcNAc residues from α-anomers[2–4] and, more importantly, with β-D-ManNAc units from the respective β-counterparts (Scheme 1).[5]

For α-D-*hexopyranosidulose oximes* of type I, ample evidence has accumulated that invariably the *Z* geometry is adopted with the N–OH or N–*O*-acyl group pointing toward the anomeric center. This entails the N-OR group to be essentially coplanar to the equatorial anomeric hydrogen causing a distinct deshielding and, hence, upfield shift of its ^{1}H NMR signal by up to 0.6 ppm as compared to the parent 2-ketose—a fact that has provided convenient configurational proof.[6] Similar conclusions may be derived from ^{13}C chemical shifts of the carbons vicinal to the carbonyl resp. oximinocarbonyl group, as the carbon on the same side as the N–OH exhibits a significantly larger upfield shift than the other.[1] Full conformational details have been provided by two X-ray structures, that is, I with OEt[7] and pyrazol[8] (R^2 = Ac) as anomeric substituents, disclosing the adoption of a $^{4}C_{1}$ conformation slightly flattened around *C*-2.

The same *Z*-oxime-OH geometries are observed for various 4-epimeric α-D-*lyxo* analogs of I[4b,6c,9] as well as for analogs lacking an anomeric substituent (H instead of OR^1), that is, the oximes of 1,5-anhydro-ketoses of D-*fructo*-[3a,10,11] D-*tagato*-, L-*rhamnulo*- and D-*xylulo* configuration.[1]



Scheme 1. The oximino-ulosyl donor approach for the generation of α-D-GlcNAc and β-D-ManNAc units.

In the case of β-*configurated hexopyranosidulose oximes* of type II, the N–OH or N–OR group is—in the $^{4}C_{1}$ conformation of the pyranoid ring—coplanar either to the anomeric substituent (*Z* geometry) or to the equally equatorial *C*-3 acyloxy group (*E*-oxime). Accordingly, one would expect the formation of either oxime or mixtures thereof. Indeed, there are two cases in the literature[12] where mixtures of *E*/*Z* oximes have been obtained upon oximation

☆ Part 44 of the series, sugar-derived building blocks; for Part 43, see Ref. 1.

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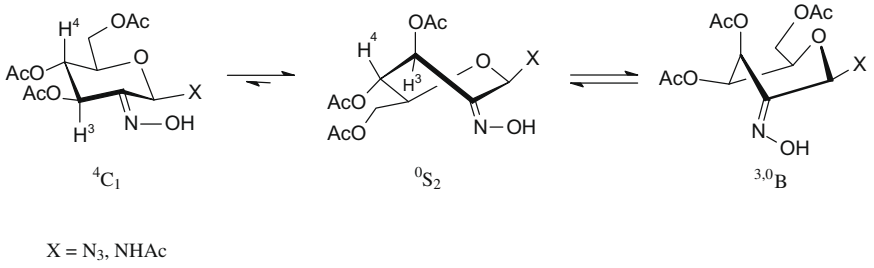
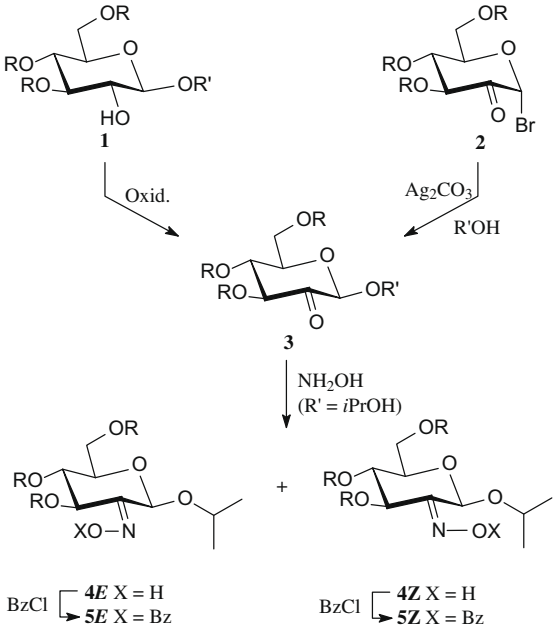


Scheme 2. Distortion of pyranoid ring conformations in two β-D-*arabino*-hexosidulose *E*-oximes as derived from X-ray data.[15,16]

of β-D-*arabino*-hexosiduloses yet they were neither separated nor the products were sufficiently characterized. On the other hand, the large number of β-D-*arabino*-hexosidulose benzoyloximes of type II, prepared via the oximino-ulosyl donor approach,[3,5,10,11,13,14] has, surprisingly, not been scrutinized as to their N–OBz geometry. Conformationally, the steric strain in the $^4C_1$ chair form of these *Z* benzoyloximes caused by the near coplanarity of N–OBz with either the anomeric (*Z* form) or the *C*-3 substituent (*E* isomer) is evaded by distortion of the pyranoid ring, as indicated by comparatively small $J_{3,4}$ and $J_{4,5}$ couplings. Obviously, the distortion operates toward adoption of the $^0S_2$ skew or twist/boat form (Scheme 2), evidenced by two X-ray structures, with N_3[15] and NHAc[16] as anomeric substituents.

In more closely addressing the *E* versus *Z* geometry in β-D-*arabino*-hexosidulose oximes, which appears to depend on their mode of generation, we here report the preparation, interconversion and unequivocal configurational assignments of five *E* and *Z* isomeric pairs, and provide evidence for the respective conformational distortions in their pyranoid rings.



a-series: R = benzoyl; b-series: R = pivaloyl; c-series: R = benzyl; R' = alkyl, glycosyl

Scheme 3. Generation and oximation of β-D-*arabino*-hexopyranosiduloses.

2. Results and discussion

2.1. Oximation of β-D-hexopyranosiduloses: *E*/*Z* mixtures

As β-D-hexopyranosiduloses are readily prepared either by oxidation of 2-OH-free β-D-glucosides **1**→**3**[17] or by Ag_2CO_3-promoted alcoholysis of α-ulosyl bromides **2**→**3**,[5] a standard procedure for generating the respective oximes is their direct oximation by exposure to hydroxylamine. Despite several examples in the literature,[12,18] the oximes obtained were—except for a ribose- and galactose-derived case[19]—not characterized as such, but directly subjected to reduction and N-acetylation toward the actual targets, that is, β-D-ManNAc units in oligosaccharides.

As demonstrated here with the oximation of isopropyl β-D-*arabino*-hexopyranosiduloses carrying benzoyl (**3a**), pivaloyl (**3b**), and benzyl blocking groups (**3c**) (Scheme 3), oximation under standard conditions invariably led to *E*/*Z* mixtures of the respective oximes, their proportions varying with the size of the vicinal 3-*O*-substituent: 2:1 in favor of the *E* isomer in the benzoyl derivatives **4a**, and 5:1 in the pivaloylated products **4b**. In the case of the more slender benzyl groups, that is, **3c**→**4c**, the *E*/*Z*-proportion of the oximes is reversed to 1:2.

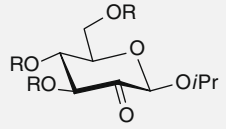
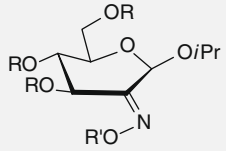
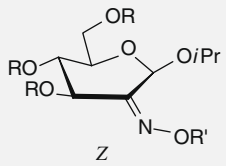
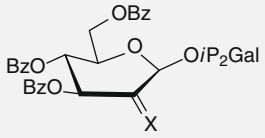
As shown by the O-benzoylation of the oxime hydroxyls (benzoyl chloride/pyridine, rt), these oximes are interconvertible, at least to equilibrium mixtures: the 5:1 *E*/*Z* mixture of pivaloylated oximes **4b**—or either of the pure *E*-**4b** and *Z*-**4b**—changes to 8:1 (^{1}H NMR), allowing the isolation of pure *E*-**5b** by fractional crystallization. All other *E*/*Z* mixtures were separated by chromatography and the individual geometrical isomers were characterized by their polarometric, ^{1}H and ^{13}C NMR data (cf. Table 1).

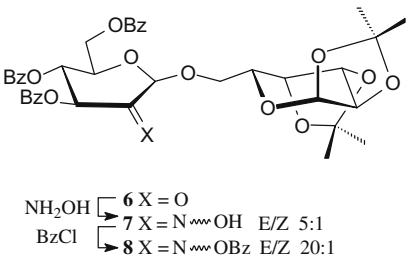
In the disaccharide-uloside **6**, oximation similarly led to *E*/*Z* oxime mixtures in favor of the *E*-isomer (5:1 ratio), which on benzoylation changes to 20:1, thus greatly facilitating the isolation of **8*E*** (Scheme 4). Its physical data clearly distinguished it from its *Z* isomer **8*Z***, which had already been prepared independently, that is, by Ag_2CO_3-promoted alcoholysis of benzoyloximino-hexosyl bromide **13a** (vide infra) with diacetone-galactose.[13]

A further indication for the $E \rightleftharpoons Z$ interconversion of the oximes came from the surprising finding that the benzoximes **5**, yet not the oximes **4** as such, show mutarotation in $CHCl_3$ (cf. Table 1) whilst rotational values are constant in dichloromethane. In the pivaloylated cases, this rotational change, apparently induced by the minime trace of acid contained in the $CHCl_3$, is distinct: $[\alpha]_D^{20}$ values (from −59.5° to +56.8° within 24 h for the *E*-benzoyloxime **5b** versus +85.5° to +60.5° for the *Z*-isomer), indicating an equilibration from each side to an approximate 1:8 *E*/*Z* mixture, hence, the *Z*-isomer being the thermodynamically more stable.

Configurational assignments. The proof of *E* and *Z* geometry for the oximes **4**, **5**, **7**, and **8** is arduous in so far, as either substituent vicinal to the oximino carbon is in an equatorial disposition, hence

Table 1
Selected ^{1}H and ^{13}C NMR data in $CDCl_3$ and $[\alpha]_D$ values for isopropyl β-D-*arabino*-hexopyranosiduloses and their *E* and *Z* oximino analogs

Compound				H-1	H-3	$J_{3,4}$	$J_{4,5}$	C-1	C-3	$[\alpha]_D^{20}$ ($CHCl_3$)
	**3a**	R = Bz[13]		5.22	5.98	10.0	8.0	78.6	77.1	−52.3
	3b	R = Piv		5.05	5.49	10.1	9.1	98.4	76.4	−22.2
	3c	R = Bn[20]		4.85	4.22	7.9	9.2	98.0	85.9	−49.0
		R	R′							
	**4a**	Bz	H	5.40	6.60	6.7	7.2	95.0	63.6	−74.1
	4b	Piv	H	5.26	6.08	6.7	7.7	94.1	69.5	−18.5
	4c	Bn	H	5.26	5.01	4.4	5.2	95.2	75.3	−35.1
	5a	Bz	Bz	5.70	6.73	6.9	7.3	95.0	64.6	−7.9→−21.2 (1h)
	5b	Piv	Bz	5.56	6.31	6.9	8.2	94.7	64.2	+85.3→+60.5 (24h)
	5c	Bn	Bz	5.54	5.06	4.9	5.4	94.9	71.3	−9.1
E										
	**4b**	Piv	H	6.04	6.01	5.7	5.5	89.6	68.7	−73.3
	4a	Bz	H	5.99	5.42	4.7	4.5	87.9	67.1	−13.5
	4c	Bn	H	5.88	4.09	2.4		90.5	75.3	−35.1
	5a	Bz	Bz	6.19	6.20	5.0	4.8	90.4	68.7	−60.7→− 21.2 (1h)
	5b	Piv	Bz	6.04	5.72	5.2	5.0	89.7	67.7	−59.9→+56.8 (24h)
	5c	Bn	Bz	6.00	4.40	2.8	5.1	90.8	74.9	−27.5
Z										
	**6**	X = O		5.40	5.99	10.0	10.1	99.3	76.7	
	7*E*	X = HO–N		5.36	6.58	7.1	8.6	97.2	63.9	
	8*E*	X = BzO–N		5.67	6.74	7.1	8.3	97.3	65.3	
	7*Z*	X = N–OH		6.02	6.00	6.0	5.6	91.7	68.7	
	8*Z*	X = N–OBz[14a]		6.09	6.26	4.3	5.3	93.2	68.7	



Scheme 4. *E*- resp. *Z*-oximes of a D-arabino-hexosulosyl-β(**1**→**6**)-D-galactose.

is sterically interfering in either arrangement with the essentially coplanar oxime–OH or –OBz groups. This steric congestion is released by distortion of the pyranoid ring, as evidenced by the comparatively small $J_{3,4}$ and $J_{4,5}$ coupling constants, sometimes even as low as $J_{3,4}$ = 2.8 (*Z*-**5c**) and $J_{4,5}$ = 4.5 Hz (*Z*-**4b**) (cf. Table 1). By contrast, the parent ulosides **3** and **6**, exhibit $J_{3,4}$ and $J_{4,5}$ couplings in the 9–10 Hz range, clearly proving the adoption of the $^4C_1$ conformation throughout. Thus—unlike their α-anomeric counterparts, where the downfield shift of the equatorial H-1 by the *Z* N–OR group relative to the parent uloside is a clear indicator of *Z* geometry[1,6]—the β-anomeric uloside/uloside oxime counterparts provide no unambiguous clues on this basis.

Aside an independent, essentially stereospecific synthesis of the *Z*-benzoyloximes of **5a**–**5c**, **8**, and **10** (vide infra: 2.2), unequivocal proof for the oxime geometries was derived from the following pieces of evidence: (i) All *Z* oximes listed out in Table 1 show their anomeric hydrogens at lower field (5.9–6.2 ppm) than their *E* isomers (5.4–5.7 ppm), obviously reflecting the deshielding through the *Z*-NOH; for H-3, not being affected by a *Z*-oriented oxime hydroxyl, the situation is reverse, its chemical shift being at higher field up to 1 ppm for the *Z* isomers relative to their *E* analogs. (ii) The NOESY spectra of *E*-**4b** and *Z*-**4b** showed the expected correlations between the N–OH proton and H-1 or H-3, that is, irradiation of H-1 in *Z*-**4b** at 5.99 ppm caused inversion not only of the H-3 and H-5 signals, but of the N–OH signal at 8.85 ppm as well. In turn, irradiation of H-3 at 5.42 ppm had no effect on the oxime-OH. In the *E*-**4b** case, the correlations between H-1 resp. H-3 and the N–OH were reverse, as expected.

In addition, we succeeded in obtaining a single crystal of the pivaloylated *E*-benzoyloxime *E*-**5b** suitable for an X-ray diffraction analysis (Fig. 1). As clearly inferable from the dihedral angles listed out in Table 2, the pyranoid ring adopts a conformation lying between a $^{1,4}B$ boat and the $^1S_5$ form, whilst the N–OBz group points away from the anomeric center, the respective torsion angle C1–C2–N2–O21 indicating the N–O bond being in antiparallel arrangement (−178.0°) to *C*1–*C*2. A more lucid substantiation of the $^{1,4}B \rightleftharpoons {}^1S_5$ conformation of *E*-**5b** is provided by the Cremer–Pople ring puckering parameters[21] (Table 3): the puckering angles ϕ= 255°, θ= 88.3°, and the amplitude Q = 0.772 Å show the excepted angles ϕ= 270° and θ= 90° for $^{1,4}B$ and ϕ= 240° and θ= 90° for $^1S_5$, respectively.[22] Atoms forming the least-squares planes of both conformations—C-2, C-3, C-5, and O-1 for the $^{1,4}B$ boat and *C*-2, *C*-3, *C*-4, and *O*-1 for the twisted $^1S_5$ form—diverge approximately 0.10 Å from the best-fit ring plane (Table 3 and Fig. 2). The identical deviation of atoms defining these planes emphasizes on the *real* conformation lying between the extremes, from which the $^{1,4}B$ is defined by ring atoms *C*-1 and *C*-4 positioned 0.62 Å and 0.67 Å above the plane, whereas the $^1S_5$ conformation is described by one atom lying above the plane (*C*-1: 0.75 Å) and one lying below (*C*-5: 0.65 Å).

On the basis of these results it may be concluded that the closely related *E* isomeric benzoximes *E*-**5a**, *E*-**5c**, and *E*-**8** will similarly adopt conformations approximating the $^{1,4}B \rightleftharpoons {}^1S_5$ forms—in the solid state. In solution, conformations appear to be different, since the dihedral angles H-3 to H-4 and H-4 to H-5 are 158.6° and 173.9°, respectively (Table 2), whilst the $J_{3,4}$ and $J_{4,5}$ couplings with 5.2 and 5.0 Hz, are comparatively too small.

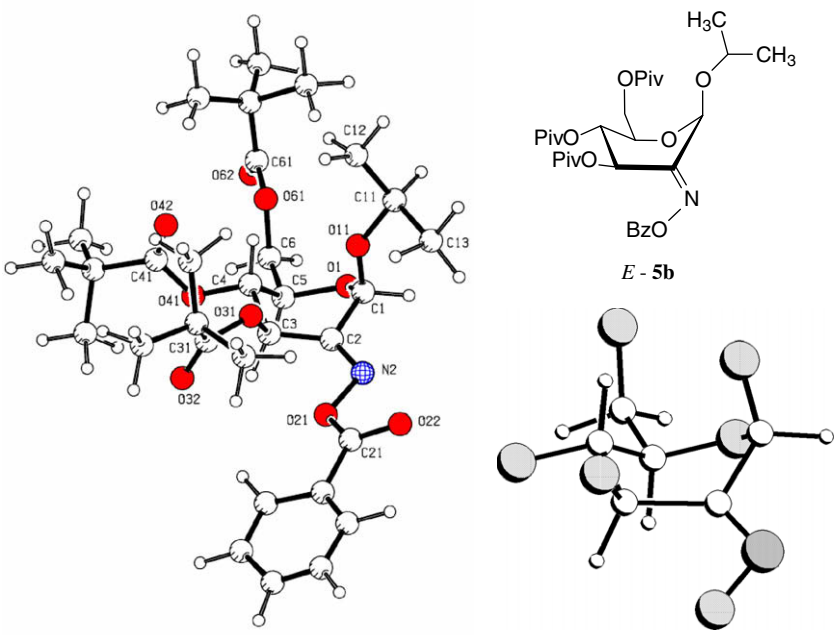


Figure 1. Perspective view of the X-ray structure of isopropyl 3,4,6-tri-*O*-pivaloyl-2*E*-benzoyloxyimino-2-deoxy-β-D-*arabino*-hexopyranoside *E*-**5b** and numbering system. To facilitate visualization of the $^{1,4}B \leftrightarrow {}^{1}S_5$ conformation of the pyranoid ring, a second view is given (right) in which pivaloyl groups and *i*-propyl substituent are omitted for clarity.

Table 2
Torsion angles in *E*-**5b**

Pyranoid ring	(°)	Substituents	(°)
C1–C2–C3–C4	+15.2	C1–C2–N2–O21	−178.8
C2–C3–C4–C5	+45.0	O11–C1–C2–N2	−111.0
C3–C4–C5–O1	−66.9	N2–C2–C3–O31	+66.0
C4–C5–O1–C1	+18.7	N2–C2–C3–C4	−173.7
C5–O1–C1–C2	+41.3	H3–C3–C4–H4	+158.6
O1–C1–C2–C3	−60.2	H4–C4–C5–H5	+173.9

Table 3
Deviations in *E*-**5b** from the least-squares best-fit plane in Å formed by four atoms and ring puckering parameters

Atom	$^{1,4}B$	$^{1}S_5$	Puckering parameters
C-1	0.62	0.75	$\phi = 255.1°$
C-2	−0.10[a]	0.10[a]	$\theta = 88.3°$
C-3	0.10[a]	−0.10[a]	
C-4	0.67	0.10[a]	$Q = 0.722$ Å
C-5	−0.10[a]	−0.65	
O-1	0.10[a]	−0.10[a]	

[a] Atoms defining a plane.

2.2. *Z*-Oximes of β-D-*arabino*-hexopyranosiduloses

Whilst the alcoholysis of 2-nitrosohexosyl chlorides invariably led to α-hexosidulose oximes,[6] the preparatively more important β-counterparts—they constitute key intermediates toward the straightforward assembly of β-D-ManNAc containing oligosaccharides[5]—are either prepared by oximation of β-D-hexosiduloses as discussed above (Section 2.1.) or by the Koenigs–Knorr type glycosidation of 2-benzoyloximinoglycosyl bromides (Scheme 5, **13**→**5**). The generation of these oximino-ulosyl donors is preparatively most straightforward, as the readily large-scale accessible 2-hydroxyglycal esters **10** smoothly undergo hydroxylaminolysis of their enol ester group,[5] and the resulting 1,5-anhydro-D-fructose oximes **11**—after O-benzoylation (→**12**)—are readily refunctionalized at the proanomeric center by photobromination **12**→**13**.[10]

In the oximes **11**–**13**, the N–OH or N–OBz group is always oriented toward the anomeric or proanomeric center as indicated in the formulae, a fact readily rationalized on the basis that the coplanar equatorial H-1 exerts considerably less steric congestion than the equally equatorial 3-OBz. Unequivocal proof for the *Z* geometry of benzoyloximinohexosyl bromides **13** as well as the respective α-

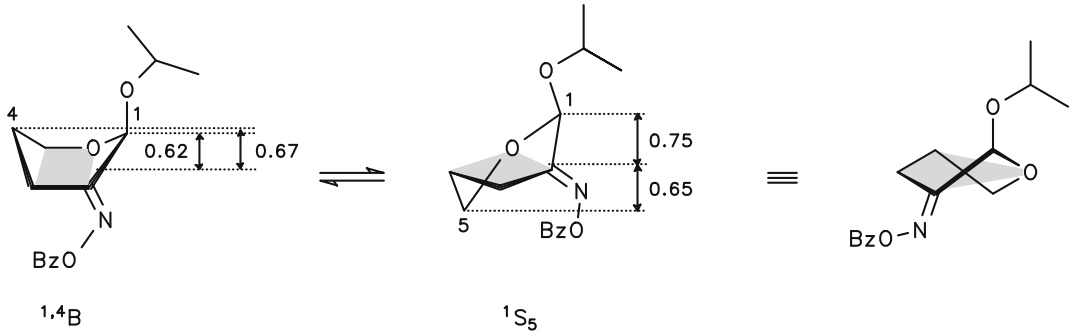
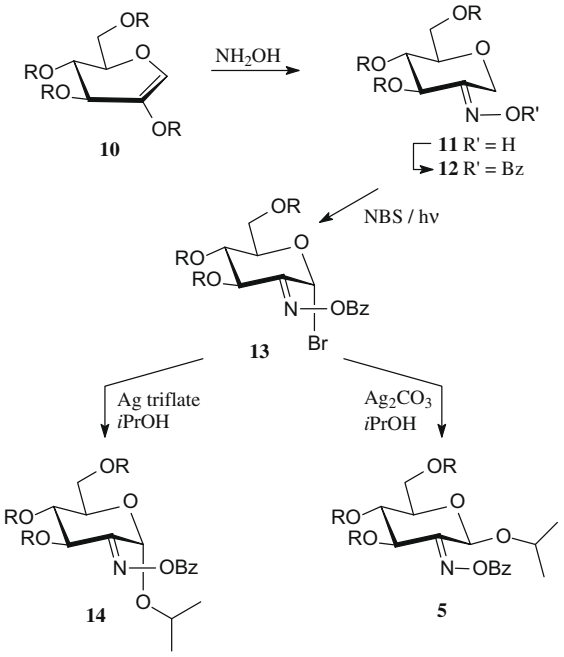


Figure 2. Graphic representation of the molecular geometry of *E*-**5b** lying between the $^{1,4}B$ boat and the twisted $^{1}S_5$ conformation. The deviations of the ring atoms from the calculated best planes (indicated by dotting) are given in Å. Substituents at *C*-3 to *C*-5 are omitted for clarity.



Scheme 5. Generation of 2*Z*-benzoyloxyimino-hexopyranosyl bromides **13** and means for their selective α-(→**14**) and β-glycosidation (→**5**).

hexosidulose oximes **14**, prepared by silver triflate-promoted alcoholysis of **13**, was convincingly derived from the downfield shift of the equatorial anomeric hydrogen induced by the coplanar N–OBz group as compared to their respective 2-oxo analogs. The data compiled in Table 4, widely scattered in the literature, provide ample evidence thereof, the shift of the equatorial anomeric hydrogen to lower field amounting to 0.6–1.2 ppm.

That the three β-configurated hexosidulose oximes **5** with R = Bz, Piv and Bn (cf. Scheme 3), prepared by Koenigs–Knorr glycosidation of the respective *Z*-benzoyloximinohexosyl bromide **13** with *i*-propanol, also have the *Z* configuration was already indicated by the distinctly uniform course of these glycosidations generating single products isolable in high yields. Unambiguous proof followed from their identity with the *Z* forms of **5a**, **5b**, and **5c** independently prepared by oximation of the glycosiduloses and subsequent benzoylation (vide supra: 2.1, Scheme 2).

On the basis of these results, an important conclusion as to the steric course of the oxime reactions depicted in Scheme 5 can be drawn: Neither the conditions of the photobromination **12**→**13** (NBS in CCl_4, *hv*, 15 min reflux) nor those for the α-glycosidation of the benzoyloximino-ulosyl bromides **13**→**14** (Ag-triflate/dioxane, *s*-collidine, rt), or the Koenigs–Knorr alcoholysis **13**→**5** (stirring with Ag_2CO_3/ROH in CH_2Cl_2, rt) affect in any way the *Z* geometry in the benzoyloximino groups.

This inference has important bearing on the large number of β-D-*arabino*-hexosidulose benzoyloximes of type II (Scheme 1), prepared via the oximino-ulosyl donor approach,[3,5,10,11,13,14] whose N–OBz geometries have, surprisingly, not been scrutinized explicitly as of now: *As the essentially β-specific Koenigs–Knorr glycosidation of the Z-benzoyloximino-ulosyl bromides proceeds with retention of configuration, they invariably have the Z geometry throughout.*

3. Conclusion

The above experimental results demonstrate, that exposure of β-D-*arabino*-hexopyranosiduloses to hydroxylamine invariably leads to *E*/*Z* mixtures of the respective oximes, their proportions varying with the size of the vicinal anomeric and 3-*O*-substituent. Their separation is readily accomplished providing the *E* and *Z* isomers in pure form thereby substantially facilitating structural and configurational assignments by NMR, notably NOESY experiments, and, in one case, by an X-ray structure. By contrast, preparation of β-D-*arabino*-hexosidulose oximes via Koenigs–Knorr glycosidation of *Z*-benzoyloximino-hexosyl bromides uniformly leads to pure *Z*-oximes, that is, without touching the steric integrity of the oxime moiety.

Due to the coplanarity in the $^4C_1$ form of the N–OH or N–OBz groups to either the anomeric (*Z* isomers) or the 3-*O* substituent (*E* counterparts), both evade this steric congestion by distortion of the pyranoid ring, as evidenced by $J_{3,4}$ and $J_{4,5}$ values much too small for diaxial arrangement of the respective hydrogens. Based on the X-ray structural data of the *E*-benzoyloxime described here and two *Z*-oximes from the literature,[15,16] these distortions can be, at least for the solid state, be specified: adoption of the $^1S_5 \rightleftharpoons {}^{1,4}B$ conformation in the case of *E*-oximes versus the $^0S_2 \rightleftharpoons {}^{3,0}B$ forms for their *Z* isomers (Fig. 3), both being closely interrelated via the $B_{2,5}$ boat form on the pseudorotational boat/skew cycle[25] of the pyranoid ring.

4. Experimental

4.1. General

Melting points were determined with a Bock hot-stage microscope and are uncorrected. Optical rotations were measured at 20 °C with a Perkin–Elmer 241 polarimeter using a cell of 1 dm path length. ^{1}H and ^{13}H NMR spectra were recorded on Bruker ARX 300 and Avance 500 instruments. Mass spectra were acquired on a Varian MAT 311 spectrometer, microanalyses on a Perkin–Elmer 240 elemental analyzer. Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F_{254} plastic sheets (Merck, Darmstadt) with detection by UV light or by spraying with 50% sul-

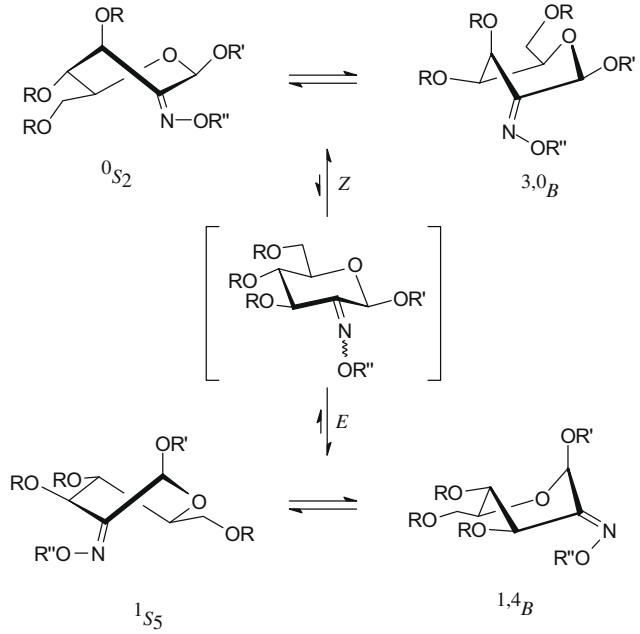
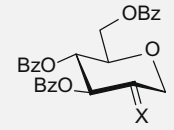
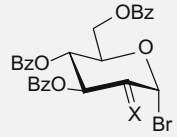
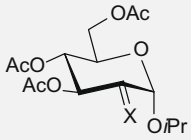
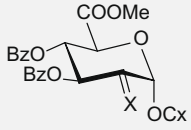
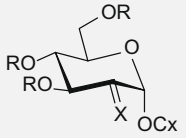


Figure 3. Pyranoid ring distortions in *E* and *Z* isomers of β-D-*arabino*-hexosidulose oximes.

Table 4
Proof of *Z* geometry of 2-ulopyranoside oximes on the basis of the deshielding, hence downfield shift, of the equatorial anomeric hydrogen by the coplanar oxime-OH or OAcyl group as compared to the parent ulosides

Compd[a]			H-1e	H-3	$J_{3,4}$	$J_{4,5}$	Downfield shift of H-1e (ppm)	Ref.
	X = O		4.57	6.19	9.8	9.8	–	11
	X = N–OH		5.17	6.02	7.2	8.1	0.60	11
	X = N–OBz		5.35	6.30	6.5	6.9	0.78	10
	R	X					–	
	Bz	O	6.52	6.54	10.4	10.4		13
	Bz	N–OBz	~7.5[b]	6.70	10.0	10.0	~1.0	10
	Piv	O	6.40	6.00	10.4	10.4	–	13
	Piv	N–OBz	7.41	6.21	10.2	10.2	1.01	c
	X = O		4.94	5.70	10.0	10.0	–	6c
	X = N–OH		6.14	5.87	9.5	9.5	1.20	6a
	X = O		5.21	6.20	10.3	10.1	–	23
	X = N–OH		6.18	6.26	9.7	9.8	0.97	23
	R	X						
	Bz	O	5.14	6.17	10.2	10.2	–	24
	Ac	N–OAc	6.02	5.76	9.7	9.9	0.88	4b

[a] Cx = cyclohexyl.
[b] Signal obscured by aromatic protons.
[c] This paper.

furic acid and charring at 140 °C for 5 min. Column chromatography was performed on Silica Gel 60 (Merck, 63–200 ppm) using the specified eluents.

4.2. Isopropyl 3,4,6-tri-*O*-pivaloyl-β-D-*arabino*-hexopyranosid-2-ulose 3b (R′ = *i*Pr)

A mixture of *i*PrOH (185 L, 1.4 mmol), silver carbonate (330 mg, 1.2 mmol) and molecular sieve (3 Å, 500 mg) in dry CH_2Cl_2 (15 mL) was stirred at room temperature for 30 min, followed by the addition of ulosyl bromide **2b**[13] (600 mg, 1.2 mmol). After stirring for another h the suspension was filtered, and the solvent was removed under reduced pressure. Trituration of the resulting syrup with Et_2O gave **3b** (540 mg, 95%) in crystalline form; mp 121–128 °C; R_f = 0.30 (4:1 CCl_4/EtOAc); $[\alpha]_D^{20}$ −22.2 (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 1.19, 1.22, 1.24 (3s, 9H each, 3C(CH_3)$_3$), 1.23, 1.31 (2d, 3H each, 2CH(CH_3)$_2$), 4.04 (m, 1H, CH(CH_3)$_2$), 4.12–4.20 (m, 2H, H-5, H-6a), 4.31 (m, 1H, H-6b), 5.05 (s, 1H, H-1), 5.36 (d, 1H, H-4), 5.49 (d, 1H, H-3); $J_{3,4}$ = 10.1, $J_{4,5}$ = 9.1, $J_{CH,CH3}$ = 6.2 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): 21.8, 23.2 (CH(CH_3)$_2$), 27.0, 27.1 (C(CH_3)$_3$), 38.8, 38.9, 39.1 (C(CH_3)$_3$), 62.4 (C-6), 69.6 (C-4), 72.7 (C-5), 72.9 (CH(CH_3)$_2$), 76.4 (C-3), 98.4 (C-1), 176.2, 177.4, 178.1 (CO*t*Bu), 191.9 (C-2). MS (FD): *m*/*z* 472 (M^+). Anal. Calcd for $C_{24}H_{40}O_9$ (472.57): C, 61.00; H, 8.53. Found: C, 61.05; H, 8.61.

4.3. Isopropyl 3,4,6,-tri-*O*-benzoyl-2-deoxy-2-hydroxyimino-β-D-*arabino*-hexopyranoside *E*-4a and *Z*-4a

A solution of isopropyl uloside **3a**[13] (5.32 g, 10 mmol) and NH_2OH·HCl (1.40 g, 20 mmol) in MeOH/pyridine (30 mL, 1:1) was stirred at room temperature for 24 h. Dilution with CH_2Cl_2 (120 mL), washing with 2 M HCl (2 × 40 mL), satd $NaHCO_3$ (20 mL), water (20 mL), drying (Na_2SO_4), and removal of the solvent in vacuo afforded a 2:1 mixture (^{1}H NMR) of *E* and *Z*-isomers (5.20 g, 95%) as a hard foam. Separation was effected by elution from a silica gel column with 20:1 toluene/EtOAc.

4.3.1. *Z*-Oxime *Z*-4a

Concentration of the first fraction (R_f 0.10 in 20:1 toluene/EtOAc) yielded *Z*-**4a** (1.43 g, 26%) as a colorless solid; $[\alpha]_D^{20}$ −73.3 (*c* 1.4, $CHCl_3$); –84.6 (*c* 1.2, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): 1.17, 1.27 (2d, 6H, C(CH_3)$_2$), 4.14 (qq, 1H, CHMe$_2$), 4.45 (dt, 1H, H-5), 4.84 (2H-d, 6-H_2), 5.86 (dd, 1H, H-4), 6.01 (d, 1H, H-3), 6.04 (s, 1H, H-1), 7.30–8.10 (m, 15H, 3C_6H_5), 8.85 (s, 1H, NOH), $J_{3,4}$ = 5.7, $J_{4,5}$ = 5.5, $J_{5,6}$ = 6.6, $J_{CH,CH3}$ = 6.1 Hz; ^{13}C NMR (75.5 MHz, $CDCl_3$): 21.4, 23.0 (C(CH_3)$_2$), 65.3 (C-6), 68.7 (C-3), 69.3 (C-4), 71.3 (CMe$_2$), 72.7 (C-5), 89.6 (C-1), 128.3–133.5 (3C_6H_5), 149.6 (C-2), 165.1, 165.3, 166.2 (3COC_6H_5), $J_{C\text{-}1,1\text{-}H}$ 171.3 Hz. Anal. Calcd for $C_{30}H_{29}NO_9$ (547.56): C, 65.81; H, 5.34; N, 2.56. Found: C, 65.68; H, 5.32; N, 2.49.

4.3.2. *E*-Oxime *E*-4a

The fraction eluted next (R_f 0.05) was treated as above to give oxime *E*-**4a** (2.80 g, 51%) as a colorless foam; $[\alpha]_D^{20}$ −74.1 (*c* 1.3, $CHCl_3$), −57.4 (*c* 1.3, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): 1.15, 1.19 (2d, 6H, C(CH_3)$_2$), 4.08 (qq, 1H, CH(CH_3)$_2$), 4.30 (ddd, 1H, H-5), 4.62 (two 1H-dd, 6-H_2), 5.40 (s, 1H, H-1), 6.04 (dd, 1H, H-4), 6.60 (d, 1H, H-3), 7.30–8.05 (m, 15H, 3C_6H_5), 8.59 (s, 1H, NOH); $J_{3,4}$ = 6.7, $J_{4,5}$ = 7.2, $J_{5,6}$ = 5.5 and 4.8, $J_{6,6}$ = 11.8, $J_{CH,CH3}$ = 6.1 Hz; ^{13}C NMR (75.5 MHz, $CDCl_3$): 21.4, 23.0 (CH(CH_3)$_2$), 63.6 (C-3), 64.5 (C-6), 69.4 (C-4), 69.9 (C(CH_3)$_2$), 72.3 (C-5), 95.0 (C-1), 125.3–133.4 (3C_6H_5), 149.5 (C-2), 165.1, 165.2, 166.3 (3COC_6H_5). Anal.

Calcd for $C_{30}H_{29}NO_9$ (547.56): C, 65.81; H, 5.34; N, 2.56. Found: C, 65.73; H, 5.28; N, 2.49.

4.4. Isopropyl 2-deoxy-2-hydroxyimino-3,4,6-tri-*O*-pivaloyl-β-D-*arabino*-hexopyranoside *E*-4b and *Z*-4b

Uloside **3b** (1.6 g, 3.4 mmol) in THF/MeOH/pyridine (100 mL, 70:20:10) was treated with $NH_2OH{\cdot}HCl$ (596 mg, 8.6 mmol) and stirred at room temperature for 2.5 h. Workup as described above for **4a** gave an amorphous 5:1 mixture (^{1}H NMR) of *E*/*Z* isomers (1.57 g, 94%). Elution from a silica gel column with 4:1 cyclohexane/EtOAc and concentration of the first fraction (R_f 0.41 in 4:1 CCl_4/EtOAc) yielded *Z*-**4b** (230 mg, 14%); $[\alpha]_D^{20}$ −13.5 (*c* 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 1.19, 1.20, 1.23 (3s and m, 33H, 3C(CH_3)$_3$, 2CH(CH_3)$_2$), 4.06 (m, 1H, H-5), 4.11 (qq, 1H, C*H*Me$_2$), 4.46 and 4.55 (two 1H-dd, 6-H$_2$), 5.24 (dd, 1H, H-4), 5.42 (d, 1H, H-3), 5.99 (s, 1H, H-1), 8.36 (br s, 1H, NOH); $J_{3,4}$ = 4.7, $J_{4,5}$ = 4.5, $J_{5,6}$ =6.0 and 7.4, $J_{6,6}$ = 11.6 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): 20.6, 22.5 (CH(CH_3)$_2$), 26.4, 26.5 (C(CH_3)$_3$), 38.1, 38.2 (*C*(CH_3)$_3$), 63.7 (C-6), 67.1 (C-3), 67.5 (C-4), 70.0 (*C*H(CH_3)$_2$), 71.7 (C-5), 87.9 (C-1), 148.1 (C-2), 176–1. 177.7 (3*t*BuCO).

***E*-4b.** The fraction eluted next (R_f 0.34 in 4:1 CCl_4/EtOAc) was processed as described above to afford *E*-**4b** as a colorless solid (720 mg, 43%); $[\alpha]_D^{20}$ −14.4 (*c* 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 1.17, 1.18, 1.22 (3s and m, 33H, 3C(CH_3)$_3$, 2CH(CH_3)$_2$), 3.96 (ddd, 1H, H-5), 4.04 (qq, 1H, C*H*(CH_3)$_2$), 4.29 and 4.34 (two 1H-dd, 6-H$_2$), 5.26 (s, 1H, H-1), 5.59 (dd, 1H, H-4), 6.08 (d, 1H, H-3), 8.46 (br s, 1H, NOH); $J_{3,4}$ = 6.7, $J_{4,5}$ = 7.7, $J_{5,6}$ = 3.9 and 5.2, $J_{6,6}$ = 12.0, $J_{CH,CH3}$ = 6.1 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): 20.8, 22.3 (CH(CH_3)$_2$), 26.4, 26.5 (C(CH_3)$_3$), 38.1, 38.2 (*C*(CH_3)$_3$), 62.7 (C-3, C-6), 67.3 (C-4), 68.5 (*C*H(CH_3)$_2$), 71.3 (C-5), 94.1 (C-1), 149.0 (C-2), 176.1, 177.7 (3*t*BuCO). MS (FD) data: *m*/*z* 487 ($M^{\bullet+}$). Anal. Calcd for $C_{24}H_{41}NO_9$ (487.59): C, 59.12; H, 8.48; N, 2.87. Found: C, 59.17; H, 8.52; N, 2.84.

NOESY experiments. Irradiation of the *Z*-**4b** signal at 5.99 (H-1) affected those at 4.06 (H-5), 5.42 (H-3), and 9.36 (N–OH), whilst, in turn, H-3 irradiation resulted in inversion of the signals for H-1, H-5, and NOH. The *E*-**4b** isomer, by contrast, showed no change in the NOH signal at 8.46 ppm on irradiation with H-1 (5.26 ppm).

4.5. Isopropyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-hydroxyimino-β-D-*arabino*-hexopyranosides *E*-4c and *Z*-4c

Uloside **3c**[13] (1.15 g, 2.3 mmol) was dissolved in THF and pyridine (50 mL each, followed by the addition of $NH_2OH{\cdot}HCl$ (1.0 g, 14.4 mmol) and stirring at ambient temperature for 1.5 h. The mixture was diluted with CH_2Cl_2 (100 mL) and poured into ice-water (200 mL). Consecutive washings of the organic phase with 2 M HCl (2 × 75 mL), satdNaHCO$_3$ solution (50 mL), and water (50 mL), drying (Na_2SO_4) and removal of the solvent in vacuo left a syrup which contained the oximes in a 1:2 *E*/*Z* ratio (^{1}H NMR). R_f (*Z*-oxime) = 0.47 (5:1 toluene/EtOAc); R_f (*E*-oxime) = 0.40.

4.5.1. *Z*-Oxime

Chromatography of the syrupy *E*/*Z*-mixture of oximes obtained on silica gel (4 × 22 cm column, elution with 10:1 toluene/EtOAc) and evaporation of the fraction eluted first to dryness in vacuo gave 485 mg (42%) of *Z*-**4c** as a colorless syrup; $[\alpha]_D^{20}$ −35.1 (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$). δ 1.16, 1.20 (2d, 6H, CH*Me*$_2$), 3.72–3.89 (m, 4H, 6-H$_2$, 5-H, 4-H), 4.09 (d, 1H, 3-H), 4.11 (m, 1H, C*H*Me$_2$), 4.44 (m, 5H, 2C*H*$_2$C$_6$H$_5$, C*H*$_{2a}$C$_6$H$_5$), 4.71 (d, 1H, C*H*$_{2b}$C$_6$H$_5$), 5.88 (s, 1H, 1-H), 7.18–7.38 (m, 15H, 3C$_6$H$_5$), 8.50 (s, 1H, NOH); $J_{3,4}$ = 2.4, J_{CH2} = 11.7, $J_{CH,CH3}$ = 6.1 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.6, 23.3. (CH*Me*$_2$), 70.4 (*C*H$_2$C$_6$H$_5$), 70.9 (C-6), 71.2 (*C*HMe$_2$), 71.9, 73.4 (2*C*H$_2$C$_6$H$_5$), 74.2 (C-5), 75.3 (C-3), 76.7 (C-4), 90.5 (C-1), 127.6–128.5, 137.6–138.4 (3C$_6$H$_5$), 152.4 (C-2). Anal. Calcd for $C_{30}H_{35}NO_6$ (505.59): C, 71.26; H 6.98; N, 2.77. Found: C, 71.15; H, 7.04; N, 2.69.

4.5.2. *E*-Oxime

Workup of the fraction eluted next gave 243 mg (21%) of *E*-**4c** as a foam. $[\alpha]_D^{20}$ −18.5 (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$). δ 1.17, 1.21 (2d, 3H each, CH*Me*$_2$), 3.72–3.91 (m, 3H, H-5, 6-H$_2$), 4.04 (dd, 1H, 4-H), 4.07 (m, 1H, C*H*Me$_2$), 4.32–4.55 (m, 4H, 2C*H*$_2$C$_6$H$_5$), 4.64, 4.72 (2d, 2H, C*H*$_2$C$_6$H$_5$), 5.01 (d, 1H, 3-H), 5.26 (s, 1H, 1-H), 7.01–7.54 (m, 15H, 3C$_6$H$_5$), 8.47 (s, 1H, NOH); $J_{3,4}$ = 4.4, $J_{4,5}$ = 5.2, J_{CH2} = 11.6, $J_{CH,CH3}$ = 6.1 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.5, 23.2 (CH*Me*$_2$), 69.5 (C-3), 69.7 (*C*H$_2$C$_6$H$_5$), 70.6 (C-6), 71.9 (*C*HMe$_2$), 72.5, 73.4 (2*C*H$_2$C$_6$H$_5$), 74.5 (C-5), 75.8 (C-4), 95.2 (C-1), 127.7–128.5, 137.6–138.5 (3C$_6$H$_5$), 152.8 (C-2). MS (FD): *m*/*z* 506 [M^++H], 445 [M^+−C$_3$H$_7$OH].

4.6. Isopropyl 3,4,6-tri-*O*-benzoyl-2-benzoyloxyimino-2-deoxy-β-D-*arabino*-hexopyranoside 5a

4.6.1. *Z*-Isomer by glycosidation of bromide 2a

Silver carbonate (138 mg, 0.50 mmol), *i*-PrOH (115 L, 1.51 mmol), and molecular sieve (4 Å, 500 mg) were suspended in CH_2Cl_2 (5 mL) and stirred for 15 min at room temperature in the dark. Bromide **12a**[10] (200 mg, 0.36 mmol) was added and stirring was continued for 2.5 h. The mixture was filtered, freed from the solvent in vacuo and eluted from a silica gel column with 10:1 toluene/EtOAc. Evaporation of the solvent afforded *Z*-**5a** (174 mg, 89%) as a colorless foam; R_f = 0.53 (10:1 toluene/EtOAc); $[\alpha]_D^{20}$ −60.7 → −21.2 (1 h, *c* 0.8, $CHCl_3$); −71.0 (*c* 1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): 1.27, 1.34 (2d, 6H, CH(CH_3)$_2$), 4.28 (qq, 1H, C*H*(CH_3)$_2$), 4.47 (dt, 1H, H-5), 4.86 (2H-d, 6-H$_2$), 5.91 (dd, 1H, H-4), 6.19 (s, 1H, H-1), 6.20 (d, 1H, H-3), 7.32–8.08 (m, 20H, 4C$_6$H$_5$); $J_{3,4}$ = 5.0, $J_{4,5}$ = 4.8, $J_{5,6}$ = 6.6, $J_{CH,CH3}$ 6.1 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): 21.6, 23.2 (CH(*C*H$_3$)$_2$), 64.8 (C-6), 68.7 (C-3), 69.2 (C-4), 71.5 (*C*H(CH$_3$)$_2$), 72.8 (C-5), 90.4 (C-1), 128.3–133.8 (4C$_6$H$_5$), 156.9 (C-2), 162.8, 164.6, 165.0, 166.0 (4*C*OC$_6$H$_5$). Anal. Calcd for $C_{37}H_{33}NO_{10}$ (651.67): C, 68.20; H, 5.10; N, 2.15. Found: C, 67.98; H, 4.99; N, 2.07.

NOESY experiments. Irradiation of the signal at 6.19 ppm (H-1) affected those at 4.47 (H-5).

4.6.2. *E* and *Z* isomer 5a by benzoylation of the *E*/*Z*-oxime mixture 4a

Benzoyl chloride (1.70 mL, 14.3 mmol) was added dropwise to a solution of oxime mixture **4a** (3.12 g, 5.71 mmol) in $CHCl_2$ (20 mL) and pyridine (2.3 mL) at 0 °C, followed by stirring for 24 h at room temperature. The solution was diluted with CH_2Cl_2 (10 mL), washed with 2 M HCl (20 mL), satd $NaHCO_3$ (20 mL), and water (20 mL), dried (Na_2SO_4) and concentrated under reduced pressure to yield a colorless syrup, comprising a 2:1 mixture of *E*-benzoyloxime (R_f = 0.10 in 3:1 CH_2Cl_2/toluene) and *Z* isomer (R_f = 0.13). Elution from a silica gel column with 2:1 CH_2Cl_2/cyclohexane and concentration of the first fraction gave 370 mg (10%) of *Z*-**5a** as a hard foam of $[\alpha]_D^{20}$ −69.9 (*c* 1, CH_2Cl_2), identical by ^{1}H and ^{13}C NMR with the product described under 4.6.1.

The fraction eluted next upon evaporation to dryness in vacuo gave the *E*-benzoyloxime *E*-**5a** (1.0 g, 27%) as an amorphous foam; $[\alpha]_D^{20}$ −7.9 → −21.5 (1 h, *c* 1.1, $CHCl_3$); −3.5 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): 1.25, 1.27 (2d, 6H, CH(CH_3)$_2$), 4.20 (qq, 1H, C*H*(CH_3)$_2$), 4.43 (ddd, 1H, H-5), 4.69 and 4.84 (two 1H-dd, 6-H$_2$), 5.70 (s, 1H, H-1), 6.19 (dd, 1H, H-4), 6.73 (d, 1H, H-3), 7.30–8.10 (m, 20H, 4C$_6$H$_5$); $J_{3,4}$ = 6.9, $J_{4,5}$ = 7.3, $J_{5,6}$ = 5.4 and 5.1, $J_{6,6}$ = 11.8, $J_{CH,CH3}$ = 6.0 Hz; ^{13}C NMR (75.5 MHz, $CDCl_3$): 21.8, 23.1 (CH(*C*H$_3$)$_2$), 64.5 (C-6), 64.6 (C-3), 69.4 (C-4), 71.0 (*C*(CH$_3$)$_2$), 72.3 (C-5), 95.0 (C-1), 127.7–133.9 (4C$_6$H$_5$), 156.3 (C-2), 163.3, 165.1, 165.2, 166.2

($4COC_6H_5$). Anal. Calcd for $C_{37}H_{33}NO_{10}$ (651.67): C, 68.20; H, 5.10; N, 2.15. Found: C, 67.97; H, 5.07; N, 2.14.

4.7. Isopropyl 2-benzoyloxyimino-2-deoxy-3,4,6-tri-*O*-pivaloyl-β-D-*arabino*-hexopyranosides *E*-5b and *Z*-5b

4.7.1. *Z*-Oxime by glycosidation of bromide 2b

A suspension of bromide **2b** (1.14 g, 1.9 mmol), silver carbonate (2.6 g, 9.4 mmol), *i*-PrOH (288 L, 3.7 mmol) and molecular sieve (3 Å, 1.5 g) in dry CH_2Cl_2 (40 mL) was stirred at room temperature for 18 h. The mixture was filtered, and freed from the solvent in vacuo to yield *Z*-**5b** (920 mg, 83%) as an amorphous product; $[\alpha]_D^{20}$ −59.5 → +56.8 (after 24 h, *c* 0.9, $CHCl_3$); –61.7 (*c* 1.1, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): 1.21, 1.24, 1.25 (three 9H-s, 6H-m, $3C(CH_3)_3$, $C(CH_3)_2$), 4.08 (m, 1H, H-5), 4.18 (m, 1H, $CH(CH_3)_2$), 4.43 and 4.52 (two 1H-dd, 6-H_2), 5.34 (dd, 1H, H-4), 5.72 (d, 1H, H-3), 6.04 (s, 1H, H-1), 7.45–8.05 (m, 5H, C_6H_5); $J_{3,4}$ = 5.2, $J_{4,5}$ = 5.0, $J_{5,6}$ = 5.7 and 7.7, $J_{6,6}$ = 11.5 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): 21.3, 23.1 ($C(CH_3)_2$), 27.0, 27.1 ($C(CH_3)_3$), 38.8, 38.9 ($C(CH_3)_3$), 64.2 (C-6), 67.7 (C-3, C-4), 71.0 ($C(CH_3)_2$), 72.7 (C-5), 89.7 (C-1), 128.3–133.7 (C_6H_5), 156.5 (C-2), 162.7 (COC_6H_5), 176.3, 176.7, 178.1 (3C*O*tBu), $J_{C\text{-}1,1\text{-}H}$ = 171.9 Hz. MS (FD): *m*/*z* 591 (M^+). Anal. Calcd for $C_{31}H_{45}NO_{10}$ (591.68): C, 62.93; H, 7.67; N, 2.37. Found: C, 62.86; H, 7.66; N, 2.36.

4.7.2. *E*-Isomer by benzoylation of *E*/*Z*-oxime mixture 4b

A solution of 1.2 g (2.4 mmol) of the 5:1-mixture of *E*-**4b**/*Z*-**4b** (as obtained under 4.4.) in CH_2Cl_2 (30 mL), pyridine (1 mL), and benzoyl chloride (685 L, 5.9 mmol) was kept at room temperature for 2 h and subsequently processed as described above (4.6.2.) to afford 1.34 g (96%) of an 8:1 *E*/*Z* amorphous mixture (^{1}H NMR). Crystallization from *i*-PrOH gave benzoyloxime *E*-**5b** as colorless prisms (1.2 g, 85%); mp 130–131 °C; $[\alpha]_D^{20}$ +85.3 → +60.5 (after 24 h, *c* 0.9, $CHCl_3$); +85.1 (*c* 1, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): 1.13, 1.16, 1.24 (3s, 27H, $3C(CH_3)_3$), 1.25, 1.30 (2d, 6H, $2C(CH_3)_2$), 4.04 (ddd, 1H, H-5), 4.13 (qq, 1H, $CHMe_2$), 4.33 and 4.37 (two 1H-dd, 6-H_2), 5.56 (s, 1H, H-1), 5.71 (dd, 1H, H-4), 6.31 (d, 1H, H-3), 7.46–8.18 (m, 5H, C_6H_5); $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.2, $J_{5,6}$ = 3.8 and 4.9, $J_{6,6}$ = 12.0, $J_{CH,CH3}$ = 6.2 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): 21.8, 23.0 ($C(CH_3)_2$), 27.0, 27.1, 27.2 ($C(CH_3)_3$), 38.7, 38.8, 38.9 ($C(CH_3)_3$), 63.2 (C-6), 64.2 (C-3), 68.0 (C-4), 70.3 (CMe_2), 72.0 (C-5), 94.7 (C-1), 127.7–134.0 (C_6H_5), 156.4 (C-2), 163.2 (COC_6H_5), 176.6, 176.7, 178.2 (*CO*tBu). MS (FD): *m*/*z* 591 (M^+), 490 (M^+−PivO/*t*$BuCO_2$). Anal. Calcd for $C_{31}H_{45}NO_{10}$ (591.68): C, 62.93; H, 7.67; N, 2.37. Found: C, 63.01; H, 7.72; N, 2.23.

Table 5
Crystal data and structure refinement for *E*-**5b**

Empirical formula	$C_{31}H_{45}NO_{10}$
Formula weight (g)	591.68
Temperature (K)	299(2)
Wavelength (Å)	0.71073
Crystal system, space group	Trigonal, R_3
A (Å)	27.692(4)
B (Å)	27.692(4)
C (Å)	11.747(4)
α (°)	90
β (°)	90
γ (°)	120
Volume (A^3)	7801.3
Z, D_{calcd} (g/cm^3)	9, 1.13
Crystal size (mm^3)	0.30 × 0.25 × 0.18
θ Range for data collection (°)	1.47–22.97
Limiting indices	$-30 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 30$, $0 \leqslant l \leqslant 12$
Reflections collected/unique [*R*(int)]	2251/2251 [0.0000]
Completeness to θ = 22.97 (%)	93.4
Maximum and minmium transmission	0.99850 and 0.9752
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2251/77/378
Goodness-of-fit on F^2	1.001
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0985, *wR*2 = 0.1949
R indices (all data)	*R*1 = 0.1011, *wR*2 = 0.2020
Extinction coefficient	1043(33)
Largest difference in peak and hole (e A^{-3})	0.439 and −0.230

X-ray diffraction analysis was carried out on an Enraf-Nonius CAD diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å). Details for crystal data, data collection, and refinement parameters are given in Table 5. Programs used for structure solution, refinement, and analysis include SHELXS97,[26] and SHELXS97.[27] The hydrogen atoms are geometrically positioned; the isopropyl group is disordered and the bonds of C9–C10, C9–C11 are fixed at 1.50 Å and not refined. Stereostructure: Figure 1; selected torsional angles: Table 2; deviations from the least-squares best-fit plane and ring puckerings: Table 3.

4.8. Isopropyl 3,4,6-tri-*O*-benzyl-2-benzoyloxyimino-2-deoxy-β-D-*arabino*-hexopyranosides *E*-5c and *Z*-5c

To a cooled (0 °C) solution of 2.8 g (5.5 mmol) of *E*/*Z*-oxime mixture **5c** in CH_2Cl_2 (50 mL) were added pyridine (1.5 mL) and dropwise benzoyl chloride (1.0 mL, 8.6 mmol), followed by stirring for 4 h at 0 °C. The mixture was then poured on ice-water (75 mL), extracted with CH_2Cl_2 (2 × 50 mL) and followed by consecutive washings of the combined organic phases with 2 M HCl (2 × 30 mL), satd $NaHCO_3$ solution (2 × 50 mL), and water. Drying (Na_2SO_4) and evaporation to dryness in vacuo gave a syrup comprising a 5:2 mixture (^{1}H NMR) of *Z*- and *E*-isomers. Separation was effected by elution from a silica gel column (3 × 18 cm) with 10:1 toluene/EtOAc.

4.8.1. *Z*-Benzoyloxime

The fraction eluted first contained *Z*-**5c** of R_f = 0.56 (5:1 toluene/EtOAc) and, upon evaporation to dryness in vacuo gave 0.77 g (23%) of a colorless syrup. $[\alpha]_D^{20}$ −27.5 (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$). δ 1.20, 1.23 (2d, 6H, $CHMe_2$), 3.75–3.94 (m, 4H, 6-H_2, 5-H, 4-H), 4.18 (m, 1H, $CHMe_2$), 4.36–4.51 (m, 5H, 3-H, $2CH_2C_6H_5$), 4.60, 4.80 (2d, 2H, $CH_2C_6H_5$), 6.00 (s, 1H, 1-H), 7.1–7.7, 8.0–8.2 (m, 20H, $4C_6H_5$); $J_{3,4}$ = 2.8, $J_{4,5}$ = 5.1, J_{CH2} = 11.7, $J_{CH,CH3}$ = 6.1 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.6, 23.3 ($CHMe_2$), 70.5 (C-6), 70.8 ($CH_2C_6H_5$), 71.7 ($CHMe_2$), 71.6, 73.4 ($2CH_2C_6H_5$), 74.3 (C-4), 74.9 (C-3), 76.5 (C-5), 90.8 (C-1), 127.6–128.5, 137.6–138.2 ($4C_6H_5$), 159.2 (C-2), 162.4 (C_6H_5CO). Anal. Calcd for $C_{37}H_{39}NO_7$ (609.69): C, 72.88; H, 6.45; N, 2.30. Found: C, 72.69; H, 6.35; N, 2.20.

4.8.2. *E*-Benzoyloxime

Further elution resulted in an *E*/*Z* mixed fraction (1.6 g, 48%) before pure *E*-**5c** (R_f = 0.46 in 5:1 toluene/EtOAc) appeared. Evaporation to dryness in vacuo afforded 0.71 g (21%) of a syrup of $[\alpha]_D^{20}$ −9.1 (*c* 1.1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$). δ 1.21, 1.23 (2d, 6H, CMe_2), 3.77–3.96 (m, 3H, 5-H, 6-H2), 4.16 (m, 1H, $CHMe_2$), 4.25 (dd, 1H, 4-H), 4.41–4.82 (m, 6H, $3CH_2C_6H_5$), 5.06 (d, 1H, 3-H), 5.54 (d, 1H, 1-H), 7.17–7.61, 7.87–8.12 (m, 20H, $4C_6H_5$); $J_{1,3}$ = 0.5, $J_{3,4}$ = 4.9, $J_{4,5}$ = 5.4, J_{CH2} = 11.6, $J_{CH,CH3}$ = 6.1 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.6, 23.1 ($CHMe_2$), 70.2 (C-6), 70.5 ($CHMe_2$), 71.2 ($CH_2C_6H_5$), 71.3 (C-3), 72.8, 73.3 ($2CH_2C_6H_5$), 74.2 (C-5), 75.4 (C-4), 94.9 (C-1), 127.7–128.5, 137.6–138.5 ($4C_6H_5$), 159.2 (C-2), 163.4 (C_6H_5CO). MS (FD): *m*/*z* 609 [M^+], 549 [M^+−$C_6H_5CH_2O$].

4.9. 1,2:3,4-Di-*O*-isopropylidene-6-*O*-(3′,4′,6′-tri-*O*-benzoyl-2-deoxy-β-D-*arabino*-hexopyranos-2-ulosyl)-D-galactopyranose 6

A mixture of diacetone–galactose[28] (210 mg, 0.81 mmol), molecular sieve 3 Å and Ag_2CO_3 (1.1 g, 4 mmol) in CH_2Cl_2

(20 mL) was stirred in the dark for 15 min followed by the addition of ulosyl iodide **2a** (with I instead of Br)[13] and continuous stirring. As no ulosyl iodide was detectable by TLC after 5 min, the mixture was diluted with 20 mL of CH_2Cl_2, filtered through Kieselgur, washed with 10% $Na_2S_2O_3$ solution (20 mL) and water (2 × 20 mL). Drying over Na_2SO_4 and removal of the solvent in vacuo gave 425 mg (83%) of a colorless foam, which turned out (^{1}H NMR) to be a mixture of keto form **6** and its hydrate (**6**·H_2O). MS (FD, 20 mA): m/z = 733 (M^++H), 717 (M^+-CH_3). ^{1}H NMR (300 MHz, $CDCl_3$) for keto form: δ 1.30–1.53 (four 3H-s, 4 Me), 3.7–4.7 (complex m, H-2′–6′-H2, 5-H, 6-H2), 5.40 (1H-s, H-1′), 5.57 (1H-d, H-1), 5.93 (1H-dd, H-4), 5.99 (1H-d, H-3); $J_{1,2}$ = 4.7, $J_{3',4'}$ = 10.0, $J_{4',5'}$ = 10.1 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$), relevant signals: δ 76.7 (C-3′), 96.2 (C-1), 99.3 (C-1′), 191.6 (C-2′).

Hydrate (**6**·H_2O): ^{1}H NMR (300 MHz, $CDCl_3$), relevant signals: 4.81 (1H-s, H-1′), 5.53 (1H-d, H-1), 5.61 (1H-dd, H-3′), 5.79 (1H-d, H-4′), $J_{3,4}$ = 5.3, $J_{4,5}$ = 9.8 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): 63.5 (C-6′), 68.4 (C-6), 75.6 (C-3′), 92.8 (C-2′), 96.2 (C-1), 102.7 (C-1′).

4.10. 1,2:3,4-Di-*O*-isopropylidene-6-*O*-(3,4,6-tri-*O*-benzoyl-2-deoxy-2-hydroxyimino-β-D-*arabino*-hexopyranosyl)-α-D-galactopyranose 7*E* and 7*Z*

Silver-alumina silicate[29] (2 g, 6.6 mmol) and freshly desiccated molecular sieve 3 Å was added to a solution of diacetone–galactose[28] (2.5 g, 9.5 mmol) followed by stirring for 30 min in the dark, and cooling to 0 °C with ice, and the addition of 4.0 g (7.2 mmol) of ulosyl bromide **2a**.[13] After 30 min, the mixture was filtered over Kieselgur and the filtrate was taken to dryness in vacuo to give uloside **6** as a colorless foam, which was dissolved in a mixture of THF (75 mL) and pyridine (150 mL), followed by the addition of NH_2OH·HCl (3.0 g, 42 mmol). Stirring at ambient temperature for 2 d, dilution with CH2Cl2 (200 mL), pouring into ice-water (200 mL), and consecutive washings of the organic phase with 2 M HCl (2 × 150 mL), satd $NaHCO_3$ solution (2 × 150 mL) and water (2 × 150 mL), drying and evaporation to dryness in vacuo left a foam comprising (^{1}H NMR) a 5:1 mixture of **7*E*** and **7*Z***. Chromatography on silica gel (5 × 30 cm column) was effected by elution with 10:1 toluene/EtOAc.

The *E*-oxime **7*E*** of R_f = 0.52 (2:1 toluene/EtOAc) was eluted first, affording 1.88 g (39%, based on **2a**) of a colorless foam; $[\alpha]_D^{20}$ −79.8 (*c* 0.98, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25, 1.32, 1.39, 1.53 (4s, 12H, C(CH_3)$_2$), 3.68 (dd, 1H, 6-H_a), 3.74 (dd, 1H, 4-H), 4.00 (m, 2H, 5-H, 6-Hb). 4.23 (m, 1H, 5′-H), 4.29 (dd, 1H, 2-H), 4.45 (dd, 1H, 3-H), 4.49 and 4.79 (two 1H-dd, 6-H_2), 5.36 (s, 1H, 1′-H), 5.54 (d, 1H, 1-H), 6.17 (dd, 1H, 4′-H), 6.58 (d, 1H, 3′-H), 7.34–8.04 (m, 15H, 3C_6H_5), 8.84 (s, 1H, NOH); $J_{3',4'}$ = 7.1, $J_{4',5'}$ = 8.6, $J_{5',6'}$ = 4.1 and 4.9, $J_{6',6'}$ = 11.9, $J_{1,2}$ = 4.9, $J_{2,3}$ = 2.4, $J_{3,4}$ = 7.9, $J_{4,5}$ = 1.5, $J_{5,6a}$ = 8.7, $J_{6,6}$ = 11.2 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 24.3, 25.2, 25.9, 26.2 (2C(CH_3)$_2$), 63.9 (C-3′), 64.1 (C-6′), 66.7 (C-6′), 67.2 (C-5′), 69.4 (C-4′), 70.7 (C-2, C-3), 70.9 (C-4), 71.9 (C-5′), 96.4 (C-1), 97.2 (C-1′), 108.9 and 109.5 (2*C*(CH_3)$_2$), 125.3–133.4 (3C_6H_5), 148.7 (C-2′), 165.1–166.2 (3COC_6H_5). Anal. Calcd for $C_{27}H_{22}NO_9$ (667.78): C, 70.14; H, 6.20; N, 2.10. Found: C, 70.03; H, 6.34; N, 2.00.

The minor product, *Z*-oxime **7*Z*** of R_f = 0.48, was eluted next: 530 mg (11%) of a colorless foam. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24, 1.32, 1.39, 1.53 (4s, 12H, C(CH_3)$_2$), 3.68 (dd, 1H, 6-H_a), 3.73 (dd, 1H, 4-H), 4.02 (m, 2H, 5-H, 6-H_b), 4.29 (dd, 1H, 2-H), 4.45 (dd, 1H, 3-H), 4.51 (m, 1H, 5′-H), 4.83 (d, 2H, 6′-H), 5.54 (d, 1H, 1-H), 5.87 (dd, 1H, 4′-H), 6.00 (d, 1H, 3′-H), 6.02 (s, 1H, 1′-H), 7.15–8.04 (m, 15H, 3C_6H_5), 8.74 (s, 1H, NOH); $J_{4',4'}$ = 6.0, $J_{4',5'}$ = 5.6, $J_{5',6'}$ = 6.3, $J_{1,2}$ = 4.9, $J_{2,3}$ = 2.4, $J_{3,4}$ = 7.8, $J_{4,5}$ = 1.5, $J_{5,6a}$ = 8.7, $J_{6,6}$ = 11.4 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 24.3, 25.0, 25.9, 26.2 (2C(CH_3)$_2$), 65.0 (C-6′), 66.7 (C-6), 67.2 (C-5), 68.7 (C-3′), 69.0 (C-4′), 70.6 (C-2, C-3), 70.9 (C-4), 72.9 (C-5′), 91.7 (C-1′), 96.4 (C-1), 108.9 and 109.5 (2*C*(CH_3)$_2$), 125.4–133.6 (3C_6H_5), 148.9 (C-2), 165.1–166.2 (3COC_6H_5).

4.11. 1,2:3,4-Di-*O*-isopropylidene-(3,4,6-tri-*O*-benzoyl-2*E*-benzoyloxyimino-2-deoxy-β-D-*arabino*-hexopyranosyl)-α-D-galactopyranose 8*E*

To a cooled (0 °C) solution of the 5:1 oxime mixture **7*E***/**7*Z*** (1.3 g, 1.7 mmol) as newly prepared according to 4.10 (cf. above) in CH_2Cl_2 (75 mL) was added dropwise 1.4 mL (12 mmol) of benzoyl chloride. Stirring was continued for 15 h allowing the mixture to warm to room temperature, followed by pouring into ice-water (50 mL) and extraction with CH_2Cl_2 (25 mL). Consecutive washing of the organic phase with 50 mL each of 2 M HCl, satd $NaHCO_3$-solution and water gave 1.56 g (94%) of a syrupy solid comprising an approximate 20:1 *E*/*Z* mixture (^{1}H NMR). It was subjected to elution from a silica gel column (4 × 22 cm) with 15:1 toluene/EtOAc. Collection of the fraction with R_f = 0.41 (5:1 toluene/EtOAc) afforded 1.23 g (74%) of **8*E*** as a colorless foamy solid of $[\alpha]_D^{20}$ −35.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29, 1.34, 1.42, 1.58 (4s, 12H, *C*(CH_3)$_2$), 3.78 (dde, 1H, 6-H_a), 3.92 (dd, 1H, 4-H), 4.07 (m, 1H, 5-H), 4.14 (dd, 1H, 6-H_b), 4.31 (dd, 1H, 2-H), 4.43 (m, 1H, 5′-H), 4.51 (dd, 1H, 3′-H), 4.63 and 4.87 (two 1H-dd, 6′-H_2), 5.55 (d, 1H, 1-H), 5.67 (s, 1H, 1′-H), 6.25 (dd, 1H, 4′-H), 6.74 (d, 1H, 3′-H), 7.25–8.12 (m, 20H, 4C_6H_5); $J_{3,4}$ = 7.1, $J_{4,5}$ = 8.3, $J_{5',6'}$ = 4.5 and 5.4, $J_{6',6'}$ = 11.9, $J_{1,2}$ = 5.0, $J_{2,5}$ = 2.4, $J_{3',4'}$ = 7.9, $J_{4',5'}$ = 1.7, $J_{5,6}$ = 6.0 and 6.3, $J_{6,6}$ = 8.9 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 24.7, 25.5, 26.3, 26.6 (2C(CH_3)$_2$), 64.6 (C-6′), 65.1 (C-3′), 67.0 (C-5), 67.5 (C-6), 69.7 (C-4′), 71.0 (C-2, C-3), 71.2 (C-4), 72.5 (C-5), 96.7 (C-1), 97.3 (C-1), 109.2 and 109.9 (2C(CH_3)$_2$), 128.0–134.1 (4C_6H_5), 155.9 (C-2′), 163.4–166.4, 171.6 (4COC_6H_5). Anal. Calcd for $C_{46}H_{45}NO_{15}$ (851.83): C, 64.85; H, 5.32; N, 1.64. Found: C, 64.73; H, 5.20; N, 1.57.

A fraction eluted last proved to be an approximate 1:2 mixture of **8*E*** and **8*Z***, from which the NMR data for the *Z* isomer could readily be gathered. They proved to be identical with those of an independently prepared **8*Z***, that is, by Ag_2CO_3-promoted glycosidation of *Z*-benzoximino-ulosyl bromide **13a** with diacetone-galactose.[14a]

4.12. 3,4,6-Tri-*O*-pivaloyl-1,5-anhydro-D-fructose *Z*-oxime 11b

To a solution of hydroxyglucal ester **10b**[13] (10 g, 20 mmol) in dry pyridine (250 mL) was added NH_2OH·HCl (9.7 g, 140 mmol). The mixture was stirred for 5 d at 70 °C, diluted with CH_2Cl_2 (300 mL) and was subsequently washed with 2 M HCl (500 mL), sat $NaHCO_3$ (200 mL), water (200 mL), and dried (Na_2SO_4). Removal of the solvent in vacuo left a crystalline residue, which was recrystallised from *i*-PrOH to yield **11b** (6.8 g, 79%) as colorless needles; mp 164–166 °C; $[\alpha]_D^{20}$ −12.3 (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 1.18, 1.20, 1.22 (3s, 27H, 3C(*CH*$_3$)$_3$), 3.73 (ddd, 1H, H-5), 3.98 (d, 1H, H-1a), 4.18–4.21 (m, 2H, 6-H_2), 5.17 (d, 1H, H-1e), 5.22 (dd, 1H, H-4), 5.56 (d, 1H, H-3), 8.56 (br s, 1H, NOH); $J_{1,1}$ = 15.4, $J_{3,4}$ = 8.3; $J_{4,5}$ = 8.7; $J_{5,6}$ = 4.8 and 2.9 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): 25.2, 27.0, 27.1 (C(*CH*$_3$)$_3$), 38.8, 38.9 (*C*(CH_3)$_3$), 61.7 (C-1), 62.4 (C-6), 68.8 (C-4), 70.5 (C-3), 76.3 (C-5), 150.8 (C-2), 176.4, 177.4, 178.3 (*CO*t*Bu*). MS (FD): m/z 429 (M^+), 328 (M^+−PivO/*t*$BuCO_2$). Anal. Calcd for $C_{21}H_{35}NO_8$ (429.51): C, 58.72; H, 8.21; N, 3.26. Found: C, 58.65; H, 8.28; N, 3.14.

4.13. 3,4,6-Tri-*O*-pivaloyl-1,5-anhydro-D-fructose *Z*-benzoyloxime 12b

A solution of oxime **11b** (2.6 g, 6 mmol) in CH_2Cl_2/pyridine (60 mL, 5:1) and benzoyl chloride (1.7 mL, 15 mmol) was stirred

for 20 h at room temperature. Dilution with CH_2Cl_2 (50 mL), washing with 2 M HCl (200 mL), satd aq $NaHCO_3$ (100 mL), and water (100 mL), drying (Na_2SO_4) and removal of the solvent in vacuo gave **12b** (2.81 g, 88%) in microcrystalline form; recrystallization of an analytic sample from *i*-PrOH afforded **12b** as colorless needles; mp 126–127 °C; $[\alpha]_D^{20}$ −44.2 (*c* 1, $CHCl_3$). ^{1}H NMR data (300 MHz, $CDCl_3$): 1.20, 1.23, 1.30 (3s, 27H, 3C(CH_3)$_3$), 3.85 (m, 1H, H-5), 4.16 (d, 1H, H-1a), 4.23 (m, 2H, 6-H_2), 5.29 (d, 1H, H-1e), 5.38 (dd, 1H, H-4), 5.78 (d, 1H, H-3), 7.44–8.01 (m, 5H, C_6H_5); $J_{1,1}$ = 15.2, $J_{3,4}$, = $J_{4,5}$ = 9.0 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): 27.0, 27.1 (C(CH_3)$_3$), 38.8, 38.9 (*C*(CH_3)$_3$), 62.0 (C-6), 62.6 (C-1), 68.2 (C-4), 70.5 (C-3), 76.7 (C-5), 128.3–133.7 (C_6H_5), 158.0 (C-2), 162.6 (*C*OC_6H_5), 176.2, 177.4, 178.1 (*C*O*t*Bu). MS (FD): *m*/*z* 533 (M^+). Anal. Calcd for $C_{28}H_{39}NO_9$ (533.62): C, 63.02; H, 7.37; N, 2.62. Found: C, 62.95; H, 7.31; N, 2.55.

4.14. 2*Z*-(Benzoyloxyimino)-2-deoxy-3,4,6-tri-*O*-pivaloyl-α-D-*arabino*-hexopyranosyl bromide 13b

A mixture of 534 mg (1 mmol) benzoyloxime **12b** and freshly recrystallized NBS (356 mg, 2 mmol) in CCl_4 (50 mL) was irradiated with a 250 W heat lamp (Hg lamp) such that gentle reflux was effected. After 30 min the resulting solution was cooled (0 °C), the succinimide was filtered off and evaporated to dryness. The residue was solved in CH_2Cl_2 (200 mL) and washed with water (100 mL). After drying (Na_2SO_4) the solvent was removed under reduced pressure to give **13b** (612 mg, quant.) as a hard foam; R_f = 0.60 (4:1 CCl_4/EtOAc); $[\alpha]_D^{20}$ +235.8 (*c* 1, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 1.21, 1.22, 1.29 (3s, 27H, 3C(CH_3)$_3$), 4.26 (2H-m, 6-H_2, 4.44 (ddd, 1H, H-5), 5.49 (dd, 1H, H-4), 6.21 (d, 1H, H-3), 7.41 (s, 1H, H-1), 7.48–8.11 (m, 5H, C_6H_5); $J_{3,4}$ = $J_{4,5}$ = 10.2, $J_{5,6}$ = 3.6 and 2.5 Hz. ^{13}C NMR (75.5 MHz, $CDCl_3$): 27.2, 27.3 (C(*C*H_3)$_3$), 39.0, 39.1 (*C*(CH_3)$_3$), 60.9 (C-6), 66.6 (C-4), 67.9 (C-3), 73.2 (C-5), 73.8 (C-1), 128.0–134.2 (C_6H_5), 155.6 (C-2), 162.1 (*C*OC_6H_5), 176.3, 177.4, 178.1 (*t*Bu*C*O). MS (FD): *m*/*z* 611, 613 (M^+).

5. Supplementary data

Crystallographic data, excluding structure factors, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication with CCDC No. 726514. Copies of the data can be obtained free of charge on application with the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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