89. Deoxy-nitrosugars

10th Communication[1])

Synthesis of Isosteric Phosphonate Analogues of Ulose-1-Phosphates

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A general approach to isosteric phosphonate analogues of ulose-1-phosphates is described. A base-catalysed chain elongation *via* a *Michael* addition of 1-deoxy-1-nitro-sugars **4**, **8**, and **16** to the vinylphosphonate **18** followed by hydrolysis of the nitro adducts gave the analogues of D-ribulose-1-phosphate, D-fructose-1-phosphate, and D-sedoheptulose-1,7-diphosphate **21**, **23**, and **27**, respectively, in high yields.

Introduction. – In recent years the interest in analogues of naturally occurring phosphates has focused on isosteric phosphonates; *i.e.* compounds in which the enzymatically cleaved C–O bond of the phosphate monoester is replaced by a non-hydrolysable C–C bond of the analogue [2] [3]. These isosteric phosphonates are potential inhibitors in metabolic processes [2] [4]. Syntheses of sugar phosphonate analogues of reducing phosphates are well-known [2] [5] [6], and syntheses of isosteric phosphonate analogues of aldose-1-phosphates have also been reported [7–10]. A general synthesis of phosphonate analogues of ulose(= ketose)-1-phosphates has so far not been described [4].

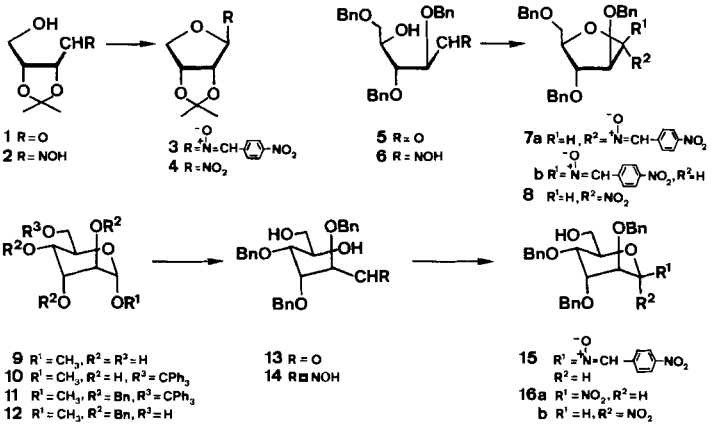
The 1-deoxy-1-nitro-aldoses are easily available compounds [11] [12] and potential precursors of isosteric phosphonate analogues of ulose-1-phosphates. Compound **4** is such a 1-deoxy-1-nitrosugar which should easily undergo *Michael* addition to a suitable vinylphosphonate such as **18** (see below, *Scheme 2*). Hydrolysis of the resulting tertiary nitro adducts would lead to the desired phosphonate skeleton such as **19**[2]). To demonstrate the scope of this approach, we synthetised the phosphonates **21**, **23** [4], and **27** as analogues of D-ribulose-1-phosphate, D-fructose-1-phosphate, and D-sedoheptulose-1,7-diphosphate, respectively. It is well-known that D-ribulose-1,5-diphosphate, D-fructose-1,6-diphosphate, and D-sedoheptulose-1,7-diphosphate play a crucial role in the *Calvin* cycle.

Results. – 2,3-*O*-Isopropylidene-D-erythrose (**1**) [17], prepared from 4,6-*O*-ethylidene-D-glucose [15] [16], was converted to the nitrosugar **4** according to the standard procedure for the preparation of 1-deoxy-1-nitrosugars [12], *i.e.* by transformation *via* the oxime **2** into the nitrone **3** and ozonolysis of this nitrone *(Scheme 1)*. The nitro sugar **4** was obtained as a single (α-D) anomer in 56% overall yield from 4,6-*O*-ethylidene-D-glu-

[1]) 9th Communication: [1].

[2]) The feasibility of this reaction sequence has so far been shown in two cases [13] [14].

Scheme 1

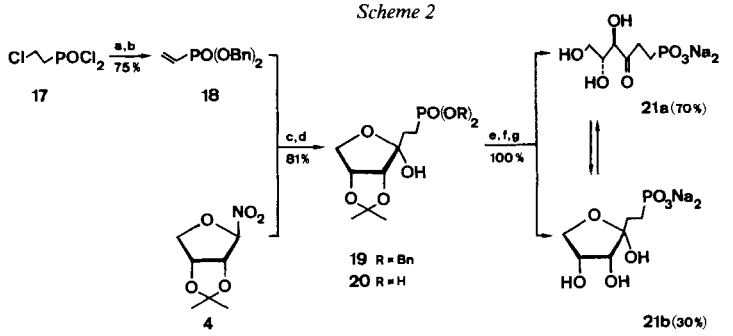


cose. Similarly, 2,3,5-tri-*O*-benzyl-D-arabinose (**5**) [18] was converted *via* **6** and **7** to the α-D-configurated nitrosugar **8** (76%). Finally, 2,3,4-tri-*O*-benzyl-D-altrose (**13**) was prepared from methyl α-D-altropyranoside (**9**) [19] by tritylation (→**10**), benzylation (→**11**), detritylation (→**12**), and acetolysis followed by deacetylation in 45% overall yield. Subsequent transformation into the nitrosugar **16** (82%) again followed the standard procedure (**13**→**14**→**15**→**16**; *Scheme 1*).

The remaining steps for the preparation of the desired phosphonic acids include a *Michael* addition of the nitrosugars **4**, **8**, and **16**, respectively, to an appropriate vinylphosphonate, the hydrolytic substitution of the NO_2- by an OH-group and a final deprotection. The use of the dibenzyl vinylphosphonate (**18**) as *Michael* acceptor allowed for a facile one-step hydrogenolytic removal of all benzyl groups in the adducts **19**, **22**, and **26**, respectively (see below, *Schemes 2–4*).

The vinylphosphonate **18** was obtained from (2-chloroethyl)phosphonic dichloride (**17**) [20][3]) by esterification with benzyl alcohol and elimination with KOH in EtOH (*Scheme 2*). In the presence of 0.25 equiv. of Bu_4NF in THF, the nitrosugar **4** reacted

Scheme 2



a) BnOH/Et_3N/r.t.; *b*) KOH/EtOH/10°; *c*) Bu_4NF/THF/r.t.; *d*) H_2O/70°; *e*) H_2/Pd/C/MeOH; *f*) H_2O/50°; *g*) *Dowex CCR-2* (Bn = $CH_2C_6H_5$)

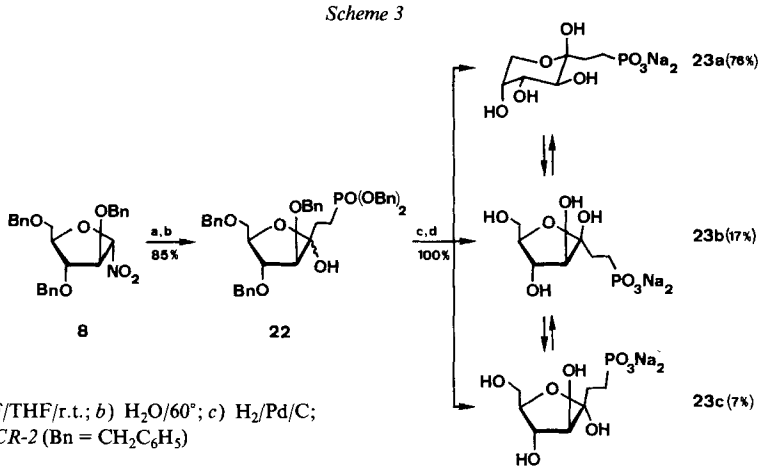
[3]) We thank Dr. *U. Gruntz, Sandoz AG*, Basel, for a generous gift of this compound.

rapidly with **18** [14] [21][4]). Direct hydrolysis of the product at 70° afforded the phosphonate **19** in 81% yield. After hydrogenolysis of **19** (Pd/C, MeOH), the phosphonic acid **20**, which is easily hydrolysable[5]), was converted to the disodium salt **21** by passage through a short column of *Dowex CCR-2* (Na^+-form) *(Scheme 2)*.

In aqueous solution, compound **21** is an equilibrium mixture of the acyclic hydroxyketone **21a** and the cyclic α-D-anomer **21b**. The ^{13}C-NMR spectra of **21a** are characterised by a C=O resonance at 214.1 ppm (*d* with ^3J(C,P) = 14.8 Hz). The corresponding ^{13}C-NMR signal of C(3) of **21b** is found at 103.6 ppm, a value typical for an α-D-anomer [22] (*d* with ^3J(C,P) = 18 Hz). The β-D-anomer of **21** could not be unequivocally identified. The relative amounts of **21a** and **21b** were determined by integration of the signals in the ^{31}P-NMR spectrum: **21a** (24.3 ppm)/**21b** (25.3 ppm) = 7:3.

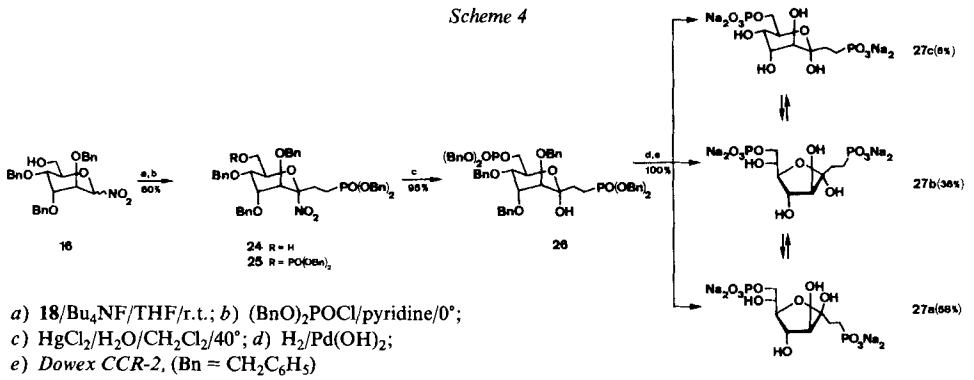
The synthesis of **23**, the analogue of D-fructose-1-phosphate, proceded in a similar way *(Scheme 3)*. *Michael* addition of the tribenzyl-1-deoxy-1-nitroarabinose **8** to **18**, followed by hydrolysis of the addition product gave **22** (83%) as a 38 (α-D): 62 (β-D)

Scheme 3



a) **18**/Bu_4NF/THF/r.t.; *b*) H_2O/60°; *c*) H_2/Pd/C;
d) *Dowex CCR-2* (Bn = $CH_2C_6H_5$)

Scheme 4



a) **18**/Bu_4NF/THF/r.t.; *b*) $(BnO)_2POCl$/pyridine/0°;
c) $HgCl_2/H_2O/CH_2Cl_2$/40°; *d*) H_2/Pd$(OH)_2$;
e) *Dowex CCR-2*, (Bn = $CH_2C_6H_5$)

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[4]) No further activation of **18** was necessary. Additions to more highly activated *Michael* acceptors such as ethyl 2-(diethylphosphono)acrylate proceded in the same way and offered no synthetic advantage.

[5]) Removal of the isopropylidene group prior to debenzylation gave **21** in a very low yield.

mixture of anomers. Hydrogenolysis of **22** (H_2/Pd-C in dioxane/H_2O[6])) and treatment with *Dowex CCR-2* (Na^+-form) afforded the sodium salt **23** in nearly quantitative yield. ^{13}C-NMR and ^{31}P-NMR analysis indicated that **23** exists as a 76:17:7 mixture of β-D-pyranose/β-D-furanose/α-D-furanose. The ^{13}C-NMR shifts coincide with those determined for D-fructose [22] and D-fructose-1,6-diphosphate [23].

We started the synthesis of the analogue **27** in the usual manner by the addition of the deoxynitroaltrose **16** to the vinylphosphonate **18** *(Scheme 4)*. The attempt to directly hydrolyse the adduct **24** gave mainly the 3,8-anhydro compound. The adduct **24** was, therefore, isolated and phosphorylated with dibenzyl phosphorochloridate [24] to **25** (60% from **16**). The hydrolysis of **25** (wet formamide, MeCN, THF/H_2O) resulted in decomposition both of the highly labile **25** and of the product **26**. Clean hydrolysis of **25** was, however, observed in the presence of $HgCl_2$ (H_2O/CH_2Cl_2) to give **26** in 95% yield. Deprotection of **26** was straightforward. Hydrogenolysis with H_2/Pd(OH)$_2$[7]) [25] at 4 atm in dioxane/H_2O and conversion of the free acid to the tetrasodium salt afforded the analogue **27** in nearly quantitative yield.

The ^{13}C-NMR data of **27** in D_2O were compared with those reported for sedoheptulose-1,7-diphosphate [26] and found to fit surprisingly well. Our assignments are based on them (see *Exper. Part*). The equilibrium composition of **27** was determined as 58:36:6 for β-D-furanose/α-D-furanose/α-D-pyranose by ^{31}P-NMR spectroscopy.

Configuration of the Nitrones and the Nitro Compounds. – Although the preparation of the nitro compounds does not require the isolation of the intermediates, we have isolated the nitrones **3**, **7a**, **7b**, and **15**, respectively, to determine their configuration at the anomeric centre with the help of ^{1}H-NMR and CD spectroscopy. The nitrone **3** was isolated as a single anomer. The ^{1}H-NMR spectrum of **3** satisfied *Imbach*'s criteria for a β-D(= 1,2-*trans*)-configuration, showing a chemical-shift difference for the isopropylidene CH_3-groups ($\Delta\delta(CH_3)$) of 0.16 ppm [27] [28] and a *s* for H–C(1) at 5.53 ppm.

Treatment of the arabinose-oxime **6** with *p*-nitrobenzaldehyde gave two compounds which were separated by fractional crystallisation to give the nitrones **7a** and **7b** in a ratio of 93:7. The major anomer shows a *s* at 5.51 ppm in the ^{1}H-NMR spectrum, whereas the corresponding signal of the minor anomer is found at 5.56 ppm as a *d* with $J(1,2) = 5.4$ Hz. These data confirm the α-D-(= 1,2-*trans*)-configuration for the major anomer and the β-D-configuration for the minor anomer.

The nitrone **15** was isolated as a single anomer. The anomeric configuration was, however, not clear from the ^{1}H-NMR spectrum (axial substituent at C(2)), since the signal for H–C(1) (5.38 ppm, $J(1,2) \leqslant 0.5$) could correspond to either anomer. A correlation of the CD spectra of the nitrones **3**, **7a**, **7b**, and **15** proved helpful *(Table 1)*. Since the absolute configuration at C(2), C(3), and C(4) is the same in the nitrones **7a**, **7b**, and **15**, respectively, the main contribution to a difference in shape of the CD spectra originates from the configuration at the anomeric centre and the different ring size (furanose and pyranose, resp.). Since the spectra of **7b** and **15** are very similar to each other, the influence of the ring size seems to be very small and the compounds must have the same anomeric configuration. The CD spectrum of the nitrone **3** shows a similar *Cotton* effect to the one of **15** and **7b** in the region of 240–260 nm. The assignment of the β-D-configura-

[6]) Hydrogenation in MeOH or EtOH proceded much faster, but led to a considerable amount of glycosides, due to the low pH of the solution.

[7]) Hydrogenolysis with 10% Pd/C *(Fluka)* was unsuccessful.

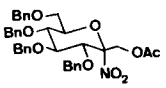
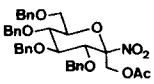
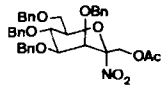
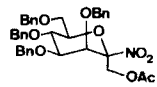
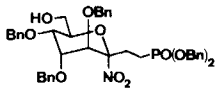
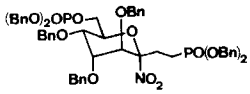
Table 1. *UV/CD Spectra (CH_2Cl_2) of Nitrones*

Nitrones	**3**	**7a**	**7b**	**15**
UV, $\lambda_{max}(\varepsilon)$	249 (10393)	253 (11511)	253 (11372)	253 (12122)
	348 (17528)	352 (17891)	355 (16774)	352 (18109)
CD, $\lambda_{max}(\Delta\varepsilon)$	255 (−0.41)	242 (+1.07)	240 (−1.53)	241 (−1.53)
		272 (−0.26)	284 (−0.09)	276 (+0.51)
	350 (−0.22)	355 (−0.97)	350 (+1.41)	341 (+3.29)

tion to **3** is also consistent with the fact that only the β-D-nitro compound was isolated after ozonolysis.

The configuration of the nitro compounds obtained by ozonolysis of the nitrones, as a rule, correspond to the one of the nitrones, unless the workup included basic conditions (*cf. Exper. Part*). Thus, the nitro-β-D-arabinose obtained from **7** anomerised completely to the more stable α-D-anomer **8** (H–C(1): 5.68 ppm, *s*), and the 1-deoxy-1-nitro-β-D-altrose **16a** anomerised to a 1:2 mixture of **16b** (H–C(1): 5.66 ppm, $J(1,2) = 1.95$) and **16a** (H–C(1): 5.38 ppm, *s*). The α-D-configuration was tentatively assigned to **16b**, based on the chemical shift of H–C(1). *Lemieux* and *Stevens* have shown that the chemical shift of the anomeric H_{eq} is virtually independent of configurational changes at other positions [29], and we consistently found chemical shift values of 5.58–5.77 for nitro α-D-compounds and 5.17–5.38 for the β-D-anomers. This assignment implies that the relative

Table 2. *Comparison of Spectral Data of* **24** *and* **25** *with those of the Similar Nitro Adducts*

Nitro compound	^{13}C-NMR [ppm] anomeric C-atom		IR [cm^{-1}] $\tilde{\nu}_{as}(NO_2)$	$[\alpha]_D^{25}$	$[\phi]_D^{25}$
	[a])	110.62	1552	+55.0°	+352.9°
	[a])	109.84	1566	+2.4°	+15.4°
	[a])	111.95	1554	+54.5°	+349.7°
	[a])	109.46	1577	−38.8°	−249.0°
	**24**	110.90	1555	+68.6°	+526.6°
	**25**	110.90	1555	+51.0°	+524.3°

[a]) See [31].

values of $J(1,2)$ of **16a** and **16b** do not correspond to the mean $J(1,2)$ values indicated by *Altona* and *Haasnoot* [30] for altropyranoses.

The chain elongation of the nitro compounds **4** and **8** by addition to **18** gave in either case mixtures of isomeric nitro adducts, which were directly hydrolysed to **19** and **22**, respectively. *Michael* addition of the mixture of anomers **16a, b** to **18**, however, led to a single isomer **24**, which was isolated. In order to establish its anomeric configuration, we correlated the spectroscopic data of **24** and **25** with the ones of similar nitro adducts prepared from D-glucose and D-mannose, respectively [31] (see *Table 2*), making use of the known fact [32] that in the IR spectrum axial NO_2-groups absorb at lower wave numbers ($\tilde{\nu}_{as}(NO_2)$ typically at 1552–1557 cm^{-1}) than equatorial NO_2-groups ($\tilde{\nu}_{as}(NO_2)$ typically at 1566–1577 cm^{-1})[8]). The nitro adduct **25** with $\tilde{\nu}(NO_2)$ 1555 cm^{-1}, therefore, possesses an axial NO_2-group. Moreover, values of the specific rotations of tertiary ethers possessing an axial NO_2-group are more positive than those with an equatorial NO_2-group *(Table 2)*. Both criteria indicate the α-D-configuration (axial NO_2-group) for **24** and **25**. The difficult solvolysis of **25** may tentatively be interpreted by invoking a stereoelectronic influence of the vicinal axial (antiperiplanar) benzyloxy group and may be correlated with the difficult oxidation of a D-manno-configurated geminal bromo-nitroso compound to the corresponding bromo-nitro compound [32] and the 'Δ-2 effect' [36].

We thank the *Swiss National Science Foundation* and *Sandoz AG*, Basel, for generous support.

Experimental Part

General. See [37]. Compounds on TLC were detected by spraying the plates with a 0.02M soln. of I_2 in 10% aq. H_2SO_4, or by dipping the plates in 10% phosphomolybdic acid in EtOH followed by heating at *ca.* 200°. Free phosphonic acids on TLC were detected by dipping the plates in vanilline reagent (1 g vanilline, 400 ml MeOH, 100 ml 50% H_2SO_4) and then heated at about 200°. UV spectra were measured with a *Perkin-Elmer-555* spectrophotometer in CH_2Cl_2. IR spectra were measured with a *Perkin-Elmer 298* spectrometer (5% $CHCl_3$, unless otherwise specified). ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR spectra were recorded on a *Varian-HA-100* (^{13}C(25.2 MHz)), *Varian-XL-200* (^{1}H(200 MHz), ^{13}C(50 MHz), ^{31}P(80 MHz)), or *Bruker-AM-400* spectrometer (^{1}H(400 MHz), ^{13}C(100.6 MHz), ^{31}P(160 MHz)); $CDCl_3$ solns. unless otherwise specified; δ's in ppm relative to TMS (for ^{1}H-NMR and ^{13}C-NMR) as internal standard or relative to H_3PO_4 (for ^{31}P-NMR) as external reference (uncorrected). Mass spectra were recorded on a *Varian 112S* (EI: 70 eV; CI: isobutan) and a *Varian 711* spectrometer (FAB, bombardement with 8-keV Xe-atoms, glycerol matrix).

Dibenzyl Vinylphosphonate (**18**). At 0°, (2-chloroethyl)phosphonic dichloride (**17**; 10.42 g, 71.38 mmol) was slowly added to benzyl alcohol (17.73 ml, 171.3 mmol) and Et_3N (39.8 ml, 285.5 mmol) in abs. Et_2O (300 ml). After stirring at r.t. for 2 h, H_2O (200 ml) was added and the org. layer was washed with dil. HCl (3 × 100 ml), dil. $NaHCO_3$ (3 × 100 ml), and H_2O. Drying ($MgSO_4$) and evaporation *i.v.* afforded 24.0 g of crude dibenzyl (2-chloroethyl)phosphonate. A soln. of this material in abs. EtOH (150 ml) was slowly added to a soln. of KOH (3.21 g, 57.1 mmol) in abs. EtOH (100 ml) at −10°, followed by stirring at 0° for 1 h. Usual workup and chromatography (toluene/AcOEt 3:1) afforded 15.43 g (75%) of **18**. R_f (toluene/AcOEt 1:1) 0.36, b.p. 171°/0.23 Torr. IR (film): 3480*m* (br.), 3090*m*, 3070*m*, 3030*m*, 3010*m*, 2950*m*, 2890*m*, 1960*w*, 1890*w*, 1815*w*, 1720*w*, 1610*m*, 1590*w*, 1500*s*, 1455*s*, 1400*s*, 1380*s*, 1240*s* (br.), 1060–960*s* (br.), 920*s*, 870–820*s* (br.), 740*s*, 700*s*. ^{1}H-NMR (200 MHz): 7.33 (*m*, 10H); 6.60–5.70 (*m*, 3H); 5.2 (*d*, J(H, P) = 8.1, 2 PhCH_2). ^{13}C-NMR (25 MHz): 136.0 (*d*, J(C, P) = 6.4); 135.5 (*dt*, J(C,P) = 1.5); 128.4 (*d*); 128.2 (*d*); 127.7 (*d*); 125.5 (*dd*, J(C, P) = 185.2); 67.3 (*dt*, J(C, P) = 5.6). ^{31}P-NMR (80 MHz): 18.9. Anal. calc. for $C_{16}H_{17}O_3P$ (288.28): C 66.66, H 5.94, P 10.74; found: C 66.35, H 5.83, P 10.70.

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[8]) A similar difference for $\tilde{\nu}$(–N≡C) in the IR spectra of anomeric glycosyl isocyanides has been reported [33–35].

2,3-O-Isopropylidene-D-erythrose (**1**). A mixture of crude D-erythrose (15.09 g, 0.1 mol) [16], abs. acetone (400 ml), and anh. $FeCl_3$ (1 g, 5 mol-%) [17] was stirred at r.t. under anh. conditions for 48 h. Then $Na_2CO_3 \cdot 10H_2O$ (50 g) was added, and stirring was continued for 2 h at r.t. After filtration through *Celite* and drying ($MgSO_4$) the soln. was concentrated *i.v.* to afford 18.2 g of crude **1** [38] as an oil. R_f (hexane/AcOEt 1:2) 0.46.

2,3-O-Isopropylidene-D-erythrose-oxime (**2**). A soln. of crude **1** (18.2 g) in abs. MeOH (50 ml) was added to a mixture of $NH_2OH \cdot HCl$ (16.07 g, 231 mmol) and $NaOCH_3$ (11.24 g, 208 mmol) in abs. MeOH (250 ml). After stirring at r.t. for 2 h, MeOH was removed *i.v.* (bath temp. 40°). The residue was diluted with H_2O and AcOEt, and the H_2O-phase was extracted with AcOEt (4 × 100 ml). Drying ($MgSO_4$) and concentration *i.v.* afforded 20.83 g of crude **2** as a thick sirup. For analysis, a small amount of **2** was crystallised (hexane/AcOEt). M.p. 90–94°, R_f (hexane/AcOEt 1:2) 0.23. IR (KBr): 3400*s*, 3210*s*, 3090*s*, 3015*m*, 3000*s*, 2940*s*, 2900*m*, 1660*w*, 1630*w*, 1440*m*, 1420*m*, 1385*s*, 1340*m*, 1300*m*, 1270*s*, 1260*s*, 1230*s*, 1165*s*, 1130*m*, 1110*m*, 1080*s*, 1050*s*, 990*m*, 960*m*, 930*m*, 915*s*, 890*s*, 840*s*, 800*m*, 705*m*. ^{1}H-NMR (200 MHz): (*Z*)-oxime: 6.95 (*d*, *J* = 4.53, H–C(1)); 5.29 (*dd*, *J* = 7.1, 4.5, H–C(2)); 4.56–4.48 (*m*, H–C(3)); 3.71–3.50 (*m*, 2H–C(4)); 2.8 (br. *s*, OH); 1.53, 1.39 (2*s*, each 3H, 2 CH_3); (*E*)-oxime: 7.46 (*d*, *J* = 7.46, H–C(1)); 4.74 (*dd*, *J* = 7.13, H–C(2)); 4.42–4.34 (*m*, H–C(3)); 3.71–3.50 (*m*, 2H–C(4)); 2.80 (br. *s*, OH); 1.53, 1.39 (*s*, each 3H, 2 CH_3); integral over H–C(1) signals: (*E*/*Z*) = 1:2. ^{13}C-NMR (25 MHz): (*Z*)-oxime: 150.4 (*d*); 110.2 (*s*); 79.6 (*d*); 72.5 (*d*); 62.4 (*t*); 27.6, 25.1 (2*q*); (*E*)-oxime: 148.5 (*d*); 110.5 (*s*); 79.8 (*d*); 76.1 (*d*); 61.5 (*t*); 27.9, 25.4 (2*q*). MS (EI): 160 (5, $M^+ - 15$), 98 (9), 70 (21), 59 (65), 43 (100). Anal. calc. for $C_7H_{13}NO_4$ (175.19): C 47.99, H 7.48, N 7.99; found: C 47.78, H 7.50, N 7.87.

N-(*p-Nitrophenylmethylidene*)-*2,3-O-isopropylidene-β-D-erythrofuranosylamine* N-*Oxide* (**3**). A mixture of crude **2** (20.83 g), *p*-nitrobenzaldehyde (26.2 g, 173 mmol), TsOH (50 mg) and Drierite (50 g) in abs. CH_2Cl_2 (250 ml) was stirred at r.t. under anh. conditions for 2 h and then filtered through *Celite*. For analysis, a small amount of **3** was washed with 10% aq. $NaHSO_3$ soln. (4×) and H_2O (3×) and then dried ($MgSO_4$). Concentration *i.v.* and crystallisation (EtO_2/hexane) afforded analytically pure **3**. M.p. 155–157°, R_f (hexane/AcOEt 1:2) 0.52, $[\alpha]_D^{25} = -133.8°$ ($CHCl_3$, *c* = 0.93). UV: 249 (10393), 348 (17528). IR (KBr): 3100*w*, 3090*w*, 3000*m*, 1600*s*, 1565*s*, 1515*s*, 1415*m*, 1385*s*, 1355*s*, 1220*s*, 1140*s*, 1110*s*, 1100*s*, 1055*s*, 865*s*, 755*m*, 730*m*, 695*m*. ^{1}H-NMR (200 MHz): 8.41, 8.26 (2*d*, *AA'BB'*, *J* = 9, 2H each, C_6H_4); 7.78 (*s*, NO=CH); 5.53 (*s*, H–C(1)); 5.30 (*d*, *J* = 5.8, H–C(2)); 5.00 (*dd*, *J* = 5.8, 3.4, H–C(3)); 4.46 (*dd*, *J* = 10.2, 3.8, H_{exo}–C(4)); 4.35 (*d*, *J* = 10.2, H_{endo}–C(4)); 1.54, 1.38 (2*s*, each 3H, 2 CH_3). ^{13}C-NMR (50 MHz): 147.8 (*s*); 135.1 (*s*); 130.0 (*d*); 129.0 (*d*); 123.6 (*d*); 113.1 (*s*); 104.4 (*d*); 84.4 (*d*); 80.1 (*d*); 76.8 (*t*); 26.2 (*q*); 24.6 (*q*). MS (Cl): 309 ($M^+ + 1$). Anal. calc. for $C_{14}H_{16}N_2O_6$ (308.29): C 54.54, H 5.23, N 9.08; found: C 54.45, H 5.17, N 9.20.

1-Deoxy-2,3-O-isopropylidene-1-nitro-β-D-erythrose (**4**). The filtered CH_2Cl_2 soln. of the crude nitrone **3** was diluted with CH_2Cl_2 (250 ml) and cooled to −50°. O_3 was bubbled through the soln. until disappearance of **3** (monitored by TLC (hexane/AcOEt 1:2)). The soln. was purged with N_2 (30 min at −50°, then 30 min at r.t.), washed with 10% aq. $NaHSO_3$ (3 × 200 ml) and H_2O (3 × 200 ml), dried ($MgSO_4$), and concentrated *i.v.* Chromatography (hexane/AcOEt 10:1) and crystallisation (Et_2O/hexane) afforded 11.12 g (52.6%, from 4,6-*O*-ethylidene-D-glucose) of **4**. M.p. 42.5–43.5°, R_f (hexane/AcOEt 10:1) 0.18, $[\alpha]_D^{25} = -116.0°$ (*c* = 0.96, $CHCl_3$). IR: 3015*m*, 3000*s*, 2860*s*, 2840*s*, 2800*m*, 1775*s*, 1460*s*, 1385*s*, 1380*s*, 1350*m*, 1310*m*, 1270*s*, 1150*s*, 1105*s*, 1080*s*, 1050*s*, 980*s*, 940*s*, 860*s*. ^{1}H-NMR (200 MHz): 5.73 (*s*, H–C(1)); 5.02 (*d*, *J* = 6.0, H–C(2)); 4.93 (*dd*, *J* = 6.0, 3.0, H–C(3)); 4.48 (*dd*, *J* = 11.0, 3.0, H_{exo}–C(4)); 4.40 (*d*, *J* = 11.0, H_{endo}–C(4)); 1.52 (*s*, CH_3); 1.36 (*s*, CH_3). ^{13}C-NMR (25.2 MHz): 113.9 (*s*); 111.5 (*d*); 85.9 (*d*); 79.4 (*d*); 78.2 (*t*); 26.2 (*q*); 24.7 (*q*). MS (Cl): 190 ($M^+ + 1$), 174 ($M^+ - 15$), 143 ($M^+ - 46$). Anal. calc. for $C_7H_{11}NO_5$ (189.2): C 44.45, H 5.86, N 7.40; found: 44.69, H 6.00, N 7.68.

*Dibenzyl 1,2-Dideoxy-4,5-O-isopropylidene-α-D-*erythro*-3-hexulofuranose-1-phosphonate* (**19**). $Bu_4NF \cdot 3H_2O$ (2.08 g, 6.60 mmol) was added in one portion to a stirred mixture of **4** (5.00 g, 26.43 mmol) and **18** (7.62 g, 26.43 mmol) in THF (80 ml) at 0°. After having stirred at r.t. for 1 h, H_2O (25 ml) and sat. aq. $NaHCO_3$ soln. (20 ml) were added and the mixture was heated at 70° for 2–3 h. Usual workup, chromatography (hexane/AcOEt 1:2) and crystallisation (Et_2O/hexane) afforded 9.60 g (81%) of **19**. M.p. 82.5–83.5°, R_f (hexane/AcOEt 1:2) 0.16, $[\alpha]_D^{20} = -25.1°$ (*c* = 1.1, $CHCl_3$, *t* = 45 min). IR: 3300*s* (br.), 3090*w*, 3070*w*, 3030*w*, 2990*s*, 2940*s*, 2880*m*, 1950*w*, 1880*w*, 1810*w*, 1605*w*, 1590*w*, 1495*m*, 1455*s*, 1380*s*, 1375*s*, 1320*m*, 1270–1190*s* (br.), 1095*s*, 1060–970*s* (br.), 920*s*, 860*s*. ^{1}H-NMR (400 MHz): α-D-anomer: 7.35 (*m*, 10H); 5.08–4.92 (*m*, 2 PhCH_2); 4.84 (*dd*, *J* = 6.0, 3.9, H–C(5)); 4.38 (*d*, *J* = 6.0, H–C(4)); 4.06 (*dd*, *J* = 10.3, 3.9, H_{exo}–C(6)); 3.90 (*d*, *J* = 10.3, H_{endo}–C(6)); 2.34–1.88 (*m*, 2H–C(1), 2H–C(2)); 1.44 (*s*, CH_3); 1.31 (*s*, CH_3); β-D-anomer: 4.68 (*m*, H–C(5)); 4.61 (*d*, *J* = 4.6, H–C(4)); 3.84 (*d*, *J* = 12, H_{endo}–C(6)); 3.46 (*dd*, *J* = 12, 4.7, H_{exo}–C(6)); 1.75 (*m*, 2H–C(2), 2H–C(1)); 1.54, 1.35 (2*s*, each 3H, 2 CH_3). ^{13}C-NMR (25.2 MHz): α-D-anomer: 136.1 (*d*, *J*(C, P) = 6.3); 128.4 (*d*); 128.2 (*d*); 127.7 (*d*); 112.1 (*s*); 106.0 (*d*, *J*(C, P) = 14.3); 84.6 (*d*); 80.8 (*d*); 70.8 (*t*); 67.4 (*dt*, *J*(C, P) = 6.4); 67.3 (*dt*, *J*(C, P) = 6.4); 27.9 (*dt*, *J*(C,

P) = 4.7), 26.3 (*q*); 24.9 (*q*); 20.4 (*dt*, *J*(C, P) = 141.5); β-D-anomer: 128.6 (*d*); 128.0 (*d*); 127.9 (*d*); 113.5 (*s*); 81.1 (*d*); 79.8 (*d*); 68.2 (*t*); 28.1 (*dt*, *J*(C, P) = 2.2); 26.1 (*q*); 24.7 (*q*); 19.6 (*dt*, *J*(C, P) = 143.3). ^{31}P-NMR (80 MHz): 35.6 (α), 34.3 (β), α/β = 91.2:8.8. MS (CI): 449 (M^+ + 1), 431 ((M^+ + 1) − 18), 373, 341. Anal. calc. for $C_{23}H_{29}O_7P$ (448.46): C 61.60, H 6.52, P 2.10; found: C 61.64, H 6.42, P 1.95.

*1,2-Dideoxy-4,5-*O*-isopropylidene-*α*-*D*-erythro-3-hexulofuranose-1-phosphonic Acid* (**20**). Ester **19** (1.00 g, 2.23 mmol) was treated with H_2 and 10% Pd/C (100 mg, *Fluka*) in MeOH (20 ml) at r.t. and under normal pressure for 2 h. Filtration and evaporation afforded 589 mg (100%) of crystalline **20**. M.p. 128–129°, R_f (PrOH/NH_3/H_2O 4:3:1) 0.54, $[\alpha]_D^{25}$ = −54.4° (*c* = 0.88, MeOH, *t* = 13 min). IR (KBr): 3380*s* (br.), 2995*s*, 2920*s*, 2700*s* (br.), 2300*m* (br.), 1630*w* (br.), 1430*m*, 1390*m*, 1380*m*, 1325*m*, 1280*s*, 1240*s*, 1210*s*, 1180*s*, 1150*s*, 1095*s*, 1050*s*, 1000*s*,940*s*, 890*m*, 860*s*, 835*m*, 820*m*, 785*m*. ^{1}H-NMR (200 MHz, (D_6)DMSO): 7.80 (br. *s*, 3 OH); 4.80 (*dd*, *J* = 5.9, 3.7, H−C(5)); 4.23 (*d*, *J* = 5.9, H−C(4)); 3.82 (*dd*, *J* = 10.0, 3.7, H_{exo}−C(6)); 3.70 (*d*, *J* = 10.0, H_{endo}−C(6)); 1.95–1.50 (*m*, 2H−C(1), 2H−C(2)); 1.35 (*s*, CH_3); 1.24 (*s*, CH_3). ^{13}C-NMR (100 MHz, (D_6)DMSO): 111.1 (*s*); 105.8 (*d*, *J*(C, P) = 15.6); 84.5 (*d*); 80.2 (*d*); 69.9 (*t*); 28.4 (*t*); 26.2 (*q*); 24.8 (*q*); 22.0 (*dt*, *J*(C, P) = 145.8). ^{31}P-NMR (160 MHz, (D_6)DMSO): 29.5. MS (FAB): 291 (*M* + Na), 313 (*M* − 1 + 2Na), 335 (*M* − 2 + 3Na). Anal. calc. for $C_9H_{17}O_7P$ (268.21): C 40.31, H 6.39, P 11.55; found: C 39.95, H 6.35, P 11.30.

*Disodium 1,2-Dideoxy-*D*-erythro-3-hexulose-1-phosphonate* (**21**). A soln. of **20** (3.00 g, 11.2 mmol) in 200 ml H_2O was kept at 50° for 24 h. The mixture was concentrated *i.v.* to 40 ml and passed through a column of *Dowex CCR-2* (Na^+-form). The effluent was lyophilised and then dried *i.v.* over P_2O_5. Yield: 3.10 g (100%) of **21**. R_f (PrOH/NH_3/H_2O 4:3:1) 0.35, $[\alpha]_D^{25}$ = −16.3° (*c* = 1.19, H_2O). ^{1}H-NMR (200 MHz, D_2O): 4.38 (*d*, *J* = 5.3, H−C(4)); 4.05 (*q*, *J* = 5.3, H−C(5)); 3.66 (*m*, 2H−C(6)); 2.87 (*m*, 1H); 1.76 (*m*, 3H), other isomers: 4.5–3.5 (*m*). ^{13}C-NMR (100 MHz, D_2O): acyclic form: 214.1 (*d*, *J*(C, P) = 14.8, C(3)); 77.6 (*d*); 72.7 (*d*); 61.6 (*t*, C(6)); 34.8 (*t*, C(2)); 22.2 (*dt*, *J*(C, P) = 135.2, C(1)); α-D-anomer: 103.6 (*d*, *J*(C, P) = 18.0, C(3)); 77.2 (*d*); 71.9 (*d*); 62.6 (*t*, C(6)); 33.8 (*t*, C(2)); 22.5 (*dt*, *J*(C, P) = 133.0, C(1)). ^{31}P-NMR (160 MHz, D_2O): 25.3 (α-D-anomer); 24.3 (acyclic form); integral approx. 3:7 for α-D/acyclic form. MS (FAB): 387 (*M* + Na + gly), 365 (*M* + 1 + gly), 343 (*M* + 2 − Na + gly), 321 (*M* + 3 − 2Na + gly), 295 (*M* + Na), 273 (*M* + 1), 251 (*M* + 2 − Na), 229 (*M* + 3 − 2Na). Anal. calc. for $C_6H_{11}Na_2O_7P$ (272.10): C 26.48, H 4.07, P 11.38; found: C 26.57, H 4.30, P 11.20.

*2,3,5-Tri-*O*-benzyl-*D*-arabinose-oxime* (**6**). In one portion, 2,3,5-tri-*O*-benzyl-D-arabinose (**5**; 20.0 g, 47.56 mmol) [18] was added to a soln. of NaOMe (from 1.64 g (71.34 mmol) of Na) and $H_2NOH \cdot HCl$ (6.61 g, 95.12 mmol) in abs. MeOH (130 ml). The heterogenous mixture was then stirred at r.t. for 2 h under anh. conditions. Evaporation of MeOH *i.v.*, extraction of the residue with CH_2Cl_2 (3 × 200 ml), drying ($MgSO_4$), and evaporation afforded 22 g (quantitative) of **6** as a viscous sirup. R_f (toluene/AcOEt 2:1) 0.31. For analysis, a small amount of **6** was purified by chromatography (toluene/AcOEt 2:1). R_f (toluene/AcOEt 2:1) 0.31, $[\alpha]_D^{25}$ = −8.67° (*c* = 2.41, CH_2Cl_2). IR: 3580*s*, 3350*s* (br.), 3080*m*, 3060*m*, 3020*m*, 3000*s*, 2910*m*, 2860*m*, 1950*w*, 1870*w*, 1810*w*, 1605*w*, 1580*w*, 1490*w*, 1450*s*, 1390*m*, 1250–1200*m* (br.), 1080*s* (br.), 1025*s*, 910*m*. ^{1}H-NMR (200 MHz): (*E*)-oxime: 8.48 (*s*, =NOH); 7.48 (*d*, *J* = 7.92, H−C(1)); 7.37–7.22 (*m*, 15H); 4.50 (*m*, 3 *AB*, 3 PhCH_2); 4.31 (*dd*, *J* = 3.5, 8, H−C(2)); 4.06 (*m*, H−C(4)); 3.66 (*m*, 3H, H−C(3), 2H−C(5)); 3.15 (*d*, *J* = 6, OH−C(4)); (*Z*)-oxime: 8.68 (*s*, =NOH); 7.37–7.22 (*m*, 15H); 7.01 (*d*, *J* = 6.1, H−C(1)); 5.90 (*dd*, *J* = 6.1, 3.0, H−C(2)); 4.50 (*m*, 3 *AB*, 3 PhCH_2); 4.06 (*m*, H−C(4)); 3.88 (*dd*, *J* = 7.5, 3.0, H−C(3)); 3.66 (*m*, 2H−C(5)); 2.85 (*d*, *J* = 6.0, OH−C(4)). ^{13}C-NMR (50 MHz): (*E*)-oxime: 149.9 (*s*); 137.7–137.3 (3*s*); 128.4–127.7 (9*d*); 80.2 (*d*); 76.7 (*d*); 74.2 (*t*); 73.5 (*t*); 71.4 (*t*); 70.9 (*t*); 69.9 (*d*); (*Z*)-oxime: 152.1 (*s*); 137.7–137.3 (3*s*); 128.4–127.7 (9*d*); 79.2 (*d*); 73.4 (*d*); 72.5 (*t*); 71.9 (*d*); 71.0 (*t*); 69.8 (*d*); isomer ratio (*E*)/(*Z*) = 2:1. MS (EI): 435 (M^+), 418 (M^+ − 17), 344 (M^+ − 91). Anal. calc. for $C_{26}H_{29}NO_5$ (435.52): C 71.70, H 6.71, N 3.22; found: C 71.46, H 6.93, N 3.10.

N-*(p-Nitrophenylmethylidene)-2,3,5-tri-*O*-benzyl-*D*-arabinofuranosylamine* N-*Oxide* (**7**). A mixture of the crude **6** (22 g), *p*-nitrobenzaldehyde (8.62 g, 57.07 mmol), TsOH (100 mg) and Drierite (20 g) in abs. CH_2Cl_2 (200 ml) was stirred at r.t. for 2 h. Drierite was removed by filtration through *Celite* and the filtrate was concentrated *i.v.* For analysis, a small amount of **7** was washed with 10% aq. $NaHSO_3$ soln. (4×) and H_2O (3×), and then dried ($MgSO_4$). Concentration *i.v.* and fractional crystallisation (EtO_2/hexane) afforded the α-D-nitrone **7a** as the main component and a small amount of the β-D-nitrone **7b** (α/β = 93:7).

α-D-*Nitrone* **7a**. M.p. 101–103°, R_f (toluene/AcOEt 2:1) 0.61, $[\alpha]_D^{25}$ = −1.4° (*c* = 0.95, $CHCl_3$). UV: 253 (11511), 352 (17891). IR (KBr): 3100*w*, 3070*w*, 3030*w*, 2960*w*, 2880*m*, 1600*m*, 1570*m*, 1520*s*, 1500*m*, 1470*m*, 1455*m*, 1415*m*, 1350*s*, 1205*m*, 1135*m*, 1100*s*, 1000*m*, 880*m*, 865*m*, 840*m*, 760*s*, 740*s*, 705*s*. ^{1}H-NMR (200 MHz): 8.41, 8.25 (*d*, *J* = 9, *AA'BB'*, C_6H_4); 7.92 (*s*, NO=CH); 7.44–7.02 (*m*, 15H); 5.51 (*s*, H−C(1)); 4.85, 4.69 (*AB*, PhCH_2); 4.70 (*m*, 1H); 4.63 (*m*, 1H); 4.64, 4.55 (*AB*, PhCH_2); 4.42, 4.34 (*AB*, PhCH_2); 4.01 (*dd*, *J* = 2.9, 1.5, H−C(3)); 3.68 (*m*, 2H−C(5)). ^{13}C-NMR (50 MHz): 147.8 (*s*); 137.6 (*s*); 137.0 (*s*); 136.8 (*s*); 135.4 (*s*); 129.1–127.4 (12*d*); 123.5 (*d*); 102.5 (*d*); 86.3 (*d*); 85.9 (*d*); 82.4 (*d*); 73.4 (*t*); 72.2 (*t*); 71.6 (*t*); 69.6 (*t*). MS (CI): 369 (M^+ + 1). Anal. calc. for $C_{33}H_{32}N_2O_7$ (568.63): C 69.70, H 5.67, N 4.93; found: C 69.53, H 5.70, N 4.87.

β-D-Nitrone **7b**. M.p. 74–77°, R_f (toluene/AcOEt 2:1) 0.49, $[\alpha]_D^{25}$ = +27.7° (*c* = 0.53, $CHCl_3$). UV: 253 (11371), 355 (16774). IR (KBr): 3080*w*, 3040*w*, 2905*m*, 2890*m*, 1600*m*, 1575*m*, 1520*s*, 1455*m*, 1340*s*, 1260*m*, 1220*m*, 1140*s*, 1100*s*, 1035*m*, 870*m*, 760*m*, 750*m*, 705*m*, 700*m*. ^{1}H-NMR (200 MHz): 8.09 (*s*, *AA'A''A'''*, C_6H_4); 7.93 (*s*, NO=CH), 7.37–7.24 (*m*, 15H); 5.56 (*d*, *J* = 5.4, H–C(1)); 4.78, 4.57 (*AB*, PhCH_2); 4.64, 4.53 (*AB*, PhCH_2); 4.53 (*s*, PhCH_2); 4.46 (*m*, 1H); 4.23 (*m*, 2H); 3.78 (*m*, 2H). ^{13}C-NMR (50 MHz): 147.5 (*s*); 137.5, 137.4, 137.1 (3*s*); 135.6 (*s*); 130.2 (*d*); 129.1 (*d*); 128.4–127.6 (7*d*); 123.4 (*d*); 98.6 (*d*); 82.8, 82.0, 79.9 (3*d*); 74.0, 73.4, 72.3 (3*t*); 68.8 (*t*). MS (Cl): 569 (M^+ + 1). Anal. calc. for $C_{33}H_{32}N_2O_7$ (568.63): C 69.70, H 5.67, N 4.93; found: C 69.75, H 5.72, N 4.95.

2,3,5-Tri-O-benzyl-1-deoxy-1-nitro-α-D-arabinofuranose (**8**). A soln. of crude **7** in CH_2Cl_2 (350 ml) was treated with O_3 at −78° (the reaction was monitored by TLC and immediately stopped when **7** had disappeared). The soln. was purged with N_2 (first at −78° for 30 min, then at r.t. for 30 min), washed with 10% aq. $NaHSO_3$ (3 × 200 ml) and H_2O (3 × 200 ml). Drying ($MgSO_4$) and concentration *i.v.* afforded a sirup, which was treated with $NaBH_4$ (899 mg, 23.78 mmol) and anh. LiCl (1.00 g, 23.78 mmol) in abs. diglyme (80 ml) at r.t. for 3 h[9]). Usual workup and chromatography (toluene/AcOEt 70:1) afforded 16.25 g (76%) of **8** as an oil. R_f (toluene/AcOEt 30:1) 0.41, $[\alpha]_D^{20}$ = +69.5° (*c* = 0.68, $CHCl_3$). IR: 3090*m*, 3060*m*, 3030*m*, 3010*m*, 2920*m*, 2870*m*, 1950*w*, 1875*w*, 1810*w*, 1605*w*, 1565*s*, 1495*s*, 1450*s*, 1365*s*, 1310*m*, 1250*m*, 1160*s*, 1110*s*, 1030*s*, 910*m*, 690*s*. ^{1}H-NMR (200 MHz): 7.35–7.18 (*m*, 15H); 5.68 (*s*, H–C(1)); 4.72 (*d*, *AB*, *J* = 12.0, 1H, PhCH_2); 4.65 (*q*, *J* = 5.2, H–C(4)), 4.57 (*d*, *AB*, *J* = 12.0, 1H, PhCH_2); 4.55 (*s*, PhCH_2); 4.41 (br. *s*, and *d*, *J* = 3.0, PhCH_2, H–C(2), resp.); 4.03 (*dd*, *J* = 5.2, 2.5, H–C(3)); 3.64 (*d*, *J* = 5.2, 2H–C(5)). ^{13}C-NMR (25.2 MHz): 137.6 (*s*); 136.8 (*s*); 136.2 (*s*); 128.9–127.6 (8*d*); 108.9 (*d*); 87.8 (*d*); 85.7 (*d*); 82.1 (*d*); 73.4 (*t*); 72.4 (*t*); 72.0 (*t*); 68.7 (*t*). MS (Cl): 449 (M^+), 402 ($M^+ - NO_2$), 358 ($M^+ - 91$). Anal. calc. for $C_{26}H_{27}NO_6$ (449.51): C 69.47, H 6.05, N 3.12; found: C 69.23, H 6.08, N 3.33.

Dibenzyl 4,5,7-Tri-O-benzyl-1,2-dideoxy-D-arabino-3-heptulofuranose-1-phosphonat (**22**). At 0°, $Bu_4NF \cdot 3H_2O$ (1.42 g, 4.52 mmol) was added in one portion to **8** (8.13 g, 18.09 mmol) and **18** (5.47 g, 18.99 mmol) in dry THF (80 ml). After stirring at r.t. for 1 h, H_2O (80 ml) and sat. $NaHCO_3$ (20 ml) was added and the mixture heated at 60° for 24 h. Usual workup and chromatography (toluene/AcOEt 2:1) afforded 10.67 g (85%) of **22** as a colorless oil. R_f (toluene/AcOEt 2:1) 0.11, $[\alpha]_D^{25}$ = +7.2° (*c* = 0.54, $CHCl_3$). IR: 3600–3200*m* (br.), 3090*m*, 3070*m*, 3030*m*, 2990*m*, 2920*m*, 2860*m*, 1955*w*, 1875*w*, 1810*w*, 1720*w*, 1605*w*, 1580*w*, 1495*m*, 1450*s*, 1360*m*, 1250–1200*s* (br.), 1100–1000*s* (br.), 915*m*, 855*m*. ^{1}H-NMR (400 MHz): α-D-isomer: 7.40–7.10 (*m*, 25H); 5.05–4.91 (*m*, (PhCH_2O)$_2$P); 4.62–4.32 (*m*, 3 *AB*, 3 PhCH_2); 4.22 or 4.13 (*s*, OH); 4.12 (*t*, *J* = 4.5, H–C(5)); 3.98 (*q*, *J* = 4.4, H–C(6)); 3.76 (*d*, *J* = 4.5, H–C(4)); 3.54 (*dd*, *J* = 10.2, 4.5, H–C(7)); 3.47 (*dd*, *J* = 10.2, 4.0, H–C(7)); 2.20–1.90 (*m*, 2H–C(2), 2H–C(1)); β-D-isomer: 7.40–7.10 (*m*, 25H): 5.05–4.91 (*m*, (PhCH_2O)$_2$P); 4.62–4.32 (*m*, 3 *AB*, 3 PhCH_2); 4.35 (*m*, H–C(6)); 4.22 or 4.13 (*s*, OH); 3.92 (*dd*, *J* = 2.7, 1.6, H–C(5)); 3.78 (*d*, *J* = 1.6, H–C(4)); 3.55 (*d*, *J* = 9.8, H–C(7)); 3.43 (*dd*, *J* = 9.8, 7.0, H–C(7')); 2.20–1.90 (*m*, 2H–C(2), 2H–C(1)). ^{13}C-NMR (100 MHz): 138.1–136.4 (7*s*), 128.5–127.6 (13*d*); α-D-isomer: 106.5 (*d*, *J*(C, P) = 16.2); 85.9 (*d*); 82.1 (*d*); 81.5 (*d*); 73.3 (*t*); 71.8 (*t*); 71.7 (*t*); 70.2 (*t*); 67.2 (*dt*, *J*(C, P) = 6.5); 27.7 (*dt*, *J*(C, P) = 3.6); 20.3 (*dt*, *J*(C, P) = 141.9); β-D-isomer: 102.7 (*d*, *J*(C, P) = 17.7); 86.2 (*d*); 83.8 (*d*); 80.1 (*d*); 73.5 (*t*); 72.5 (*t*); 72.1 (*t*); 70.8 (*t*); 67.1 (*dt*, *J*(C, P) = 6.5); 31.2 (*dt*, *J*(C, P) = 3.9); 19.8 (*dt*, *J*(C, P) = 142.8). ^{31}P-NMR (160 MHz): 35.1 (α); 34.5 (β), integral α/β = 38:62. Anal. calc. for $C_{42}H_{45}O_8P$ (708.80): C 71.17, H 6.40, P 4.37; found: C 70.48, H 6.66, P 4.20.

Disodium 1,2-Dideoxy-D-arabino-3-heptulose-1-phosphonate (**23**). A soln. of **22** (4.31 g, 6.08 mmol) in 100 ml of dioxane/H_2O 1:1 was treated with 10% Pd/C (1 g, *Fluka*) under H_2 at normal pressure. After 3 h, the catalyst was removed by filtration and the soln. was concentrated to half of the volume. After dilution with H_2O (50 ml) and addition of fresh catalyst (1 g), the hydrogenation was continued for 3 h. Filtration, concentration *i.v.* to 40 ml, treatment with *Dowex CCR-2* (Na^+-form) and lyophilisation afforded 1.87 g (100%) of **23**. R_f (PrOH/NH_3/H_2O 4:3:1) 0.24, $[\alpha]_D^{25}$ = −38.1° (*c* = 0.86, H_2O). ^{1}H-NMR (200 MHz, D_2O): 4.06–3.63 (*m*, 5H); 1.95 (*m*, 2H); 1.59 (*m*, 2H). ^{13}C-NMR (50 MHz, D_2O); due to line broadening of ^{13}C-signals of **23** (pH 8, D_2O), the data of the free acid are reported (pH 1–2, D_2O): β-D-pyranose: 98.9 (*d*, *J*(C, P) = 17.4, C(3)); 70.5 (*d*, C(5)); 70.1 (*d*, C(6)); 69.5 (*d*, C(4)); 63.9 (*t*, C(7)); 31.3 (*t*, C(2)); 20.8 (*dt*, *J*(C, P) = 136.2, C(1)); β-D-furanose: 102.4 (*d*, *J*(C, P) = 19.0, C(3)); 80.9 (*d*, C(6)); 78.9 (*d*, C(4)); 75.2 (*d*, C(5)); 62.9 (*t*, C(7)); 31.3 (*t*, C(2)); 21.2 (*dt*, *J*(C, P) = 136.8, C(1)); α-D-furanose: 106.3 (*d*, *J*(C, P) = 19.7, C(3)); 82.6 (*d*, C(4)); 82.1 (*d*, C(6)); 77.5 (*d*, C(5)); 61.8 (*t*, C(7)); C(2) and C(1) not visible; α-D-pyranose: 99.6 (*d*, *J*(C, P) = 17.3, C(3)); additional signals at 77.0 (*d*), 72.5 (*d*), 71.6 (*d*); 71.1 (*d*); 66.7 (*d*); 31.6 (*t*); and 31.0 (*t*). ^{31}P-NMR (160 MHz, D_2O, integral): 23.1 (**23a**, 76%); 22.6 (**23b**, 17%); 21.5 (**23c**, 7%). MS (FAB): 303 (*M* + 1). Anal. calc. for $C_7H_{13}Na_2O_8P$ (302.13): C 27.82, H 4.33, P 10.25; found: C 27.30, H 4.45, P 9.86.

Methyl 6-O-Trityl-α-D-altropyranoside (**10**). A mixture of methyl α-D-altropyranoside **9** [19] (20.68 g, 106.5 mmol), trityl chloride (44.53 g, 159.7 mmol), and 4-(N,N-dimethylamino)pyridine (650 mg, 5 mol-%) in abs.

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[9]) To transform any benzoates formed by overoxidation into the corresponding easily removed alcohols [12].

pyridine (50 ml) and abs. $CHCl_3$ (100 ml) was stirred at r.t. for 12 h. Dilution with H_2O (100 ml), extraction with $CHCl_3$ (4 × 150 ml), drying ($MgSO_4$), and evaporation *i.v.*, followed by co-evaporation with EtOH and toluene (5×) afforded a yellow sirup. Chromatography (hexane/AcOEt 1:6) and drying *i.v.* gave 36.6 g (79%) of **10** as a slightly yellow foam. R_f (hexane/AcOEt 1:6) 0.3.

*Methyl 2,3,4-Tri-*O*-benzyl-α-*D*-altropyranoside* (**12**). NaH (4.08 g, 169.89 mmol; *Fluka*, 60% NaH in oil) was washed with dry hexane under N_2 and then added in one portion to a soln. of **10** (14.54 g, 33.31 mmol) in abs. DMF (200 ml). After stirring at r.t. for 30 min, benzyl bromide (29.7 ml, 249.82 mmol) was added dropwise over 30 min to the cooled (0°) suspension, followed by stirring at r.t. for 24 h. Excess NaH was then destroyed with abs. MeOH (15 ml) and the mixture treated with 13 g of thiourea at r.t. for 2 h. Evaporation of DMF *i.v.* and usual workup furnished 31.1 g of crude **11**. This material was treated with $ZnBr_2$ (150 g, 0.66 mol) [39] in abs. CH_2Cl_2 (70 ml) for 3 h under vigorous stirring. Cautious addition of abs. MeOH (30 ml) followed by H_2O (100 ml), usual workup, and chromatography (toluene/AcOEt 3:1) afforded 13.30 g (86%) of **12** as an oil. R_f (toluene/AcOEt 3:1) 0.14, $[\alpha]_D^{25} = +82.2°$ ($c = 1.03$, $CHCl_3$). IR: 3590*m*, 3510*m* (br.), 3090*m*, 3070*m*, 3030*m*, 3000*s*, 2930*s*, 2880*s*, 1955*w*, 1875*w*, 1810*w*, 1730*w*, 1605*w*, 1585*w*, 1495*m*, 1455*s*, 1370*m*, 1250–1200*m* (br.), 1140*s*, 1090*s* (br.), 1040*s*, 990*s*. ^{1}H-NMR (400 MHz): 7.33 (*m*, 15H); 4.67 (*s*, H–C(1)); 4.66 (*d*, A^1B^1, $J = 12.5$, 1H, PhCH_2); 4.54 (*d*, A^1B^1, $J = 12.5$, 1H, PhCH_2); 4.50 (*d*, A^2B^2, $J = 12.0$, 1H, PhCH_2); 4.49 (*d*, A^3B^3, $J = 12.0$, 1H, PhCH_2); 4.43 (*d*, A^2B^2, $J = 12.0$, 1H, PhCH_2); 4.40 (*d*, A^3B^3, $J = 12.0$, 1H, PhCH_2); 4.15 (*dt*, $J = 8.0, 4.0$, H–C(5)); 3.85 (*dd*, $J = 11.0, 4.0$, H–C(6)); 3.78 (*m*, H–C(3), H–C(4), H–C(6)); 3.68 (*d*, $J = 3.0$, H–C(2)); 3.37 (*s*, CH_3O). ^{13}C-NMR (50 MHz): 138.3 (*s*); 138.0 (*s*); 137.6 (*s*); 128.4–127.5 (6*d*); 100.2 (*d*); 75.3 (*d*); 72.7 (*d*); 72.4 (*t*); 72.3 (*d*); 71.9 (*t*); 71.3 (*t*); 67.4 (*d*); 62.7 (*t*); 55.3 (*q*). MS (CI): 463 ($M^+ - 1$), 431, 415, 397. Anal. calc. for $C_{28}H_{32}O_6$ (464.56): C 72.39, H 6.94; found: C 72.18, H 6.84.

*2,3,4-Tri-*O*-benzyl-*D*-altrose* (**13**). Prepared according to [19] (yield 11.1 g (86%), from 13.3 g of **12**). M.p. 85–86°, R_f (hexane/AcOEt 1:2) 0.29, $[\alpha]_D^{25} = -64.3°$ ($c = 0.7$, $CHCl_3$). IR (KBr): 3540*s*, 3440*s* (br.), 3090*w*, 3060*m*, 3030*m*, 2970*m*, 2930*m*, 2880*m*, 1950*w*, 1815*w*, 1810*w*, 1605*w*, 1590*w*, 1495*m*, 1455*s*, 1380*m*, 1320*m*, 1280*m*, 1260*m*, 1220*m*, 1210*m*, 1080*s*, 1050*s*, 1000*s*, 950*m*, 900*m*, 860*m*, 780*m*, 750*s*, 730*s*, 700*s*. ^{1}H-NMR (200 MHz, (D_6)DMSO): 7.38–7.25 (*m*, 15H); 6.48 (*d*, $J = 7.0$, exchangeable with D_2O, OH–C(1)); 4.94 (*d*, $J = 7.0$, with D_2O: *d*, $J = 1.3$, H–C(1)); 4.70 (*d*, *AB*, $J = 12.2$, 1H, PhCH_2); 4.58 (*s*, PhCH_2); 4.53 (*d*, *AB*, $J = 12.2$, 1H, PhCH_2); 4.49 (*d*, *AB*, $J = 11.3$, 1H, PhCH_2); 4.42 (*d*, *AB*, $J = 11.3$, 1H, PhCH_2); 3.95 (*dd*, $J = 3.8, 2.7$, H–C(3)); 3.70–3.45 (*m*, 5H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 138.8 (*s*); 138.6 (*s*); 138.4 (*s*); 128.1–127.3 (7*d*); 92.4 (*d*); 76.4 (*d*); 73.9 (*d*); 73.5 (*d*); 72.8 (*d*); 72.6 (*t*); 71.9 (*t*); 70.5 (*t*); 61.3 (*t*). Anal. calc. for $C_{27}H_{30}O_6$ (450.54): C 71.98, H 6.71; found: C 72.08, H 6.71.

*2,3,4-Tri-*O*-benzyl-*D*-altrose-oxime* (**14**). Compound **13** (8.64 g, 19.17 mmol) was added in one portion to a well-stirred mixture of $NH_2OH \cdot HCl$ (2.66 g, 38.33 mmol) and NaOMe (1.86 g, 43.50 mmol) in abs. MeOH (100 ml) and stirring was continued for 9 h at r.t. MeOH was then removed *i.v.* (bath temp. 40°), the residue was extracted with AcOEt (5×) and dried ($MgSO_4$). Evaporation of the solvent *i.v.* furnished 8.90 g of crude **14** as viscous sirup. R_f (hexane/AcOEt 1:2) 0.29.

*N-(*p*-Nitrophenylmethylidene)2,3,4-tri-*O*-benzyl-β-*D*-altropyranosylamine* N-*Oxide* (**15**). A mixture of crude **14** (8.90 g, 19 mmol), *p*-nitrobenzaldehyde (3.48 g, 23.0 mmol), TsOH (36 mg, 1 mol-%), and Drierite (40 g) in abs. CH_2Cl_2 (100 ml) was stirred at r.t. for 5 h. The mixture was then filtered through *Celite* and evaporated *i.v.* For analysis, a small amount of **15** was washed with 10% aq. $NaHSO_3$ soln. (4×) and H_2O (3×), dried ($MgSO_4$), and crystallised from hexane/AcOEt. M.p. 81–84°, R_f (hexane/AcOEt 1:2) 0.40, $[\alpha]_D^{25} = +112.4°$ ($c = 0.57$, $CHCl_3$). UV: 253 (12122), 352 (18109). IR: 3605*m*, 3500*m* (br.), 3110*w*, 3090*w*, 3070*m*, 3030*m*, 3000*m*, 2930*m*, 2870*m*, 1955*w*, 1880*w*, 1810*w*, 1730*w*, 1600*w*, 1575*m*, 1520*s*, 1495*m*, 1455*s*, 1420*m*, 1340*s*, 1150*s*, 1100*s*, 900*m*, 865*s*, 840*m*. ^{1}H-NMR (200 MHz): 8.46, 8.27 (each *d*, *AA'BB'*, $J = 9.0$, C_6H_4); 7.91 (*s*, NO=CH); 7.39–7.03 (*m*, 3 *Ph*CH_2); 5.38 (*d*, $J \leq 0.5$, H–C(1)), 4.58–3.86 (*m*, 12H); 2.95 (br. *s*, OH). ^{13}C-NMR (50.3 MHz): 147.8 (*s*); 137.4 (*s*); 137.2 (*s*); 135.4 (*s*); 130.9 (*d*); 129.5 (*d*); 128.4–127.7 (8*d*); 123.6 (*d*); 93.2 (*d*); 75.5 (*d*); 74.2 (*d*); 74.0 (*t*); 72.8 (*t*); 72.1 (*d*); 71.8 (*d*); 71.5 (*t*); 62.3 (*t*). MS (CI): 599 ($M^+ + 1$). Anal. calc. for $C_{34}H_{34}N_2O_8$ (598.66): C 68.21, H 5.72, N 4.68; found: C 68.20, H 5.65, N 4.61.

*2,3,4-Tri-*O*-benzyl-1-deoxy-1-nitro-*D*-altropyranose* (**16**) was prepared according to the procedure indicated for **8**. Yield after chromatography (toluene/AcOEt 8.5:1): 7.26 g (82%) of oily **16** as a mixture of anomers. R_f (toluene/AcOEt 8.5:1) 0.18 and 0.13, $[\alpha]_D^{25} = +74.3°$ ($c = 0.53$, $CHCl_3$). IR: 3600*m*, 3450*w* (br.), 3090*w*, 3070*w*, 3030*m*, 3000*m*, 2930*m*, 2880*m*, 1955*w*, 1875*w*, 1815*w*, 1725*w*, 1605*w*, 1565*s*, 1495*m*, 1455*m*, 1370*m*, 1355*m*, 1330*m*, 1310*m*, 1240*m*, 1190*m*, 1165*m*, 1100*s* (br.), 1030*s*, 910*m*. ^{1}H-NMR (200 MHz): 7.39–7.11 (*m*, 15H); 5.65 (*d*, $J = 1.9$, H_α–C(1)); 5.37 (*s*, H_β–C(1)); $\alpha/\beta = 1:2$; 4.60–3.92 (*m*, 13H, all other H). ^{13}C-NMR (100 MHz): 101.1, 100.6 (2*d*, C(1) of both anomers); 76.4–70.8 (11 signals); 61.8 (*t*). MS (EI): 388 ($M^+ - 91$). Anal. calc. for $C_{27}H_{29}NO_7$ (479.53): C 67.63, H 6.09, N 2.92; found: C 67.40, H 6.20, N 2.80.

*Dibenzyl 4,5,6-Tri-O-benzyl-1,2,3-trideoxy-3-nitro-α-*D*-altro-3-octulopyranose-1-phosphonate* (**24**). $Bu_4NF \cdot 3H_2O$ (1.19 g, 3.7 mmol) was added in one portion to a cooled (0°), stirred mixture of **16** (7.23 g, 15.07 mmol) and **18** (4.34 g, 15.07 mmol) in abs. THF (95 ml). Stirring was continued for 10 min at 0°, then for 2 h at r.t. Evaporation *i.v.* and chromatography (toluene/AcOEt 2:1) afforded 8.89 g (77%) of **24** (colorless oil, **24** decomposes partially on SiO_2). R_f (toluene/AcOEt 2:1) 0.17, $[\alpha]_D^{25} = +68.6°$ ($c = 0.54$, $CHCl_3$). IR: 3600*m*, 3380*m* (br.), 3090*m*, 3060*m*, 3030*m*, 3000*s*, 2950*m*, 2920*m*, 2870*m*, 1955*w*, 1880*w*, 1810*w*, 1605*w*, 1585*w*, 1555*s*, 1495*m*, 1450*s*, 1370*m*, 1250–1200*s* (br.), 1160*m*, 1090*s*, 1050–990*s* (br.), 915*m*. ^{1}H-NMR (400 MHz): 7.45–7.10 (*m*, 25H); 5.02–4.86 (*m*, $(PhCH_2O)_2P$); 4.47, 4.31 (A^1B^1, $J = 11.8$, $PhCH_2$); 4.40, 4.23 (A^2B^2, $J = 12.4$, $PhCH_2$); 4.39, 4.30 (A^3B^3, $J = 11.7$, $PhCH_2$); 4.38 (*d*, $J = 3.6$, H–C(4)); 4.40 (*m*, H–C(7)); 3.94 (*dd*, $J = 12.5, 2.5$, H–C(8)); 3.88 (*dd*, $J = 10.3, 2.5$, H–C(6)); 3.79 (*dd*, $J = 12.5, 3.3$, H–C(8)); 3.59 (*dd*, $J = 3.6, 2.5$, H–C(5)); 2.48 (*m*, H–C(2)); 2.10 (*m*, H–C(2)); 1.90 (*m*, H–C(1)); 1.65 (br. *s*, OH); 1.55 (*m*, H–C(1)). ^{13}C-NMR (100 MHz): 137.7 (*s*); 137.2 (*s*); 136.5 (*s*); 136.2 (*s*); 128.7–127.8 (13*d*); 110.9 (*d*, J(C, P) = 13.9); 76.1 (*d*); 74.3 (*d*); 72.8 (*d*); 72.1 (*t*); 71.7 (*t*); 71.3 (*t*); 70.0 (*d*); 67.5 (*dt*, J(C, P) = 6.2); 67.30 (*dt*, J(C, P) = 7.0); 61.4 (*t*); 29.8 (*dt*, J(C, P) = 2.4); 19.4 (*dt*, J(C, P) = 145.0). ^{31}P-NMR (160 MHz): 32.2. Anal. calc. for $C_{43}H_{46}NO_{10}P$ (767.62): C 67.28, H 6.04, N 1.82, P 4.04; found: C 67.39, H 5.84, N 1.70, P 3.96.

*Dibenzyl 4,5,6-Tri-O-benzyl-8-O-(dibenzyloxyphosphoryl)-1,2,3-trideoxy-3-nitro-α-*D*-altro-3-octulopyranose-1-phosphonate* (**25**). Dibenzyl phosphorochloridate (9.47 g, 31.9 mmol) [24] was added dropwise under N_2 to a soln. of **24** (6.13 g, 7.98 mmol) in abs. pyridine (130 ml) at −30°. After 8 h at −10°, H_2O (5 ml) was added and stirring was continued for 15 min at 0°. Pyridine was removed *i.v.*, finally repeated by coevaporation with toluene. The residue was filtered through a short SiO_2 column (300 g) and then chromatographed (hexane/AcOEt 1:1) to afford 6.43 g (78%) of **25** as an oil. R_f (hexane/AcOEt 1:2) 0.39, $[\alpha]_D^{25} = +51.1°$ ($c = 0.58$, $CHCl_3$). IR: 3090*m*, 3060*m*, 3030*m*, 3000*s*, 2950*m*, 2920*m*, 2890*m*, 2870*m*, 1955*w*, 1880*w*, 1810*w*, 1730*w*, 1605*w*, 1585*w*, 1555*s*, 1495*m*, 1450*s*, 1375*m*, 1340*w*, 1330*w*, 1305*m*, 1250*s* (br.), 1155*m*, 1095*s*, 1080*s*, 1000*s* (br.), 915*m*, 870*m*, 840*m*, 690*m*. ^{1}H-NMR (400 MHz): 7.34–7.08 (*m*, 35H), 4.99, 4.98 (*d*, J(C, P) = 8.0, $(PhCH_2OPO_2)$; 4.95–4.84 (*m*, $(PhCH_2O)_2PO$); 4.49 (*dm*, $J = 10.3$, H–C(7)); 4.43, 4.25 (A^1B^1, $J = 11.9$, $PhCH_2$); 4.36, 4.16 (A^2B^2, $J = 12.2$, $PhCH_2$); 4.38 (*m*, H–C(8)); 4.36 (*d*, $J = 3.7$, H–C(4)); 4.28, 4.17 (A^3B^3, $J = 11.7$, $PhCH_2$); 4.27 (*m*, H–C(8)); 3.82 (*dd*, $J = 10.3, 2.4$, H–C(6)); 3.54 (*dd*, $J = 3.7, 2.4$, H–C(5)); 2.45 (*m*, 1H); 2.15 (*m*, 2H); 1.40 (*m*, 1H). ^{13}C-NMR (100 MHz): 137.3–135.7 (5*s*); 128.6–127.7 (7*d*); 110.9 (*d*, J(C, P) = 18.3); 76.0 (*d*); 74.3 (*t*); 72.1 (*t*); 71.4 (*t*); 71.0 (*d*); 70.9 (*d*); 69.6 (*d*); 69.2 (*t*); 67.1 (*t*); 66.0 (*t*); 29.9 (*t*); 19.0 (*dt*, J(C, P) = 143.2). ^{31}P-NMR (160 MHz): +31.95 (phosphonate), −0.33 (phosphate). Anal. calc. for $C_{57}H_{59}NO_{13}P_2$ (1028.05): C 66.59, H 5.78, N 1.36, P 5.85; found: C 66.43, H 5.76, N 1.30, P 6.03.

*Dibenzyl 4,5,6-Tri-O-benzyl-8-O-(dibenzyloxyphosphoryl)-1,2-dideoxy-*D*-altro-3-octulopyranose-1-phosphonate* (**26**). A mixture of **25** (1.00 g, 0.97 mmol), $HgCl_2$ (2.65 g, 9.7 mmol), and H_2O (1.76 ml, 97 mmol) in CH_2Cl_2 (37 ml) was heated under reflux for 3 d. CH_2Cl_2 was evaporated *i.v.*, and the residue was taken up in $CHCl_3$ and filtered. Washing with 1% aq. KI soln. at 0° (3×), then with H_2O (3×), drying ($MgSO_4$), and evaporation *i.v.* furnished a yellowish oil, which, after chromatography (hexane/AcOEt 2:3), afforded 905.8 mg (95%) of **26** as a colorless oil. R_f (hexane/AcOEt 1:2) 0.15, $[\alpha]_D^{25} = +2.3°$ ($c = 0.68$, $CHCl_3$). IR: 3440*m* (br.), 3090*w*, 3060*m*, 3030*m*, 2995*s*, 2950*m*, 2920*m*, 2890*m*, 2460*w*, 1950*w*, 1880*w*, 1810*w*, 1720*w*, 1605*w*, 1585*w*, 1495*m*, 1450*s*, 1375*m*, 1250–1200*s* (br.), 1155*m*, 1080*s* (br.), 1000*s* (br.), 915*s*. ^{1}H-NMR (400 MHz): 7.37–7.04 (*m*, 35H); 5.57 (*s*, OH); 5.01 (*dd*, $J = 7.7, 1.1$, $PhCH_2OPO_3$); 5.00 (*d*, $J = 7.8$, $PhCH_2OPO_3$); 4.92–4.87 (*m*, $(PhCH_2O)PO$); 4.68, 4.45 (A^1B^1, $J = 11.8$, $PhCH_2$); 4.45, 4.31 (A^2B^2, $J = 11.7$, $PhCH_2$); 4.31 (*m*, 2H–C(8)); 4.27, 4.20 (A^3B^3, $J = 11.9$, $PhCH_2$); 4.13 (*dm*, $J = 9.5$, H–C(7)); 3.80 (*m*, H–C(5), H–C(6)); 3.27 (*d*, $J = 3.2$, H–C(4)); 2.20, 1.70 (*m*, 2H–C(2), 2H–C(1)). ^{13}C-NMR (100 MHz): 137.7–136.1 (5*s*); 128.6–127.7 (10*d*); 97.8 (*d*, J(C, P) = 18.6); 76.5 (*d*); 74.1 (*t*); 73.8 (*d*); 73.0 (*t*); 72.2 (*t*); 71.6 (*d*); 69.2 (2*t*); 67.0–66.8 (4*t*); 29.9 (*t*); 19.1 (*dt*, J(C, P) = 143.9). ^{31}P-NMR (160 MHz): +35.0 (phosphonate); −0.5 (phosphate). Anal. calc. for $C_{57}H_{60}O_{12}P_2$ (999.05): C 68.53, H 6.05, P 6.20; found: C 67.99, H 6.43, P 6.00.

*Tetrasodium 1,2-Dideoxy-8-O-phosphonato-*D*-altro-3-octulose-1-phosphonate* (**27**). A soln. of **26** (960 mg, 0.96 mmol) in 50 ml of dioxane/H_2O 1:1 was treated with $Pd(OH)_2$/C (330 mg) [25] under 5 atm of H_2 for 3 h. After filtration and concentration of the filtrate to half of the volume, H_2O (25 ml) and fresh catalyst (300 mg) were added, and the hydrogenation was continued for 3 h. Filtration, treatment with *Dowex CCR-2* (Na^+-form), lyophilisation and drying *i.v.* over P_2O_5 afforded 438 mg (100%) of **27**. R_f ($PrOH/NH_3/H_2O$ 4:3:1) 0.16, $[\alpha]_D^{25} = +3.6°$ ($c = 0.83$, H_2O). ^{1}H-NMR (200 MHz, D_2O): 4.50–3.75 (*m*, 6H); 1.95 (*m*, 2H); 1.55 (*m*, 2H). ^{13}C-NMR (100 MHz, D_2O): *β*-D-furanose **27a**: 103.5 (*d*, J(C, P) = 11.5, C(3)); 80.9 (*d*, C(6)); 79.6 (*d*, C(4)); 75.6 (*d*, C(5)); 72.3 (*d*, C(7)); 65.0 (*t*, C(8)); 32.9 (*dt*, J(C, P) = 3.7, C(2)); 23.2 (*dt*, J(C, P) = 129.8, C(1)); α-D-furanose **27b**: 107.5 (*d*, J(C, P) = 15.7, C(3)); 83.7 (*d*, C(4)); 81.4 (*d*, C(6)); 77.4 (*d*, C(5)); 71.2 (*d*, C(7)); 65.3 (*t*, C(8)); 29.6 (*t*, C(2)); 23.2 (*dt*, J(C, P) = 129.8, C(1)); α-D-pyranose **27c**: 100.5 (*d*, C(3)); 72.1 (*d*, C(5)); 69.4 (*d*, C(7)); 68.8 (*d*,

C(4)); 64.0 (*d*, C(6)); 63.9 (*t*, C(8)); 32.1 (*t*, C(2)); 23.2 (*dt*, *J*(C, P) = 129.8, C(1)). ^{31}P-NMR (160 MHz, D_2O): 22.8 (**27b**), 22.3 (**27a**), 21.3 (**27c**); integral over phosphonate signals **27b**/**27a**/**27c** = 35.9:58.2:5.9; 5.5 (**27b**), 5.2 (**27a**), 4.7 (**27c**). MS (FAB): 457 (M + 1), 435 (M + 2 − Na), 413 (M + 3 − 2Na), 391 (M + 4 − 3Na), 369 (M + 5 − 4Na). Anal. calc. for $C_8H_{14}Na_2O_{12}P_2$ (456.10): C 21.07, H 3.09, P 13.58; found: C 20.88, H 3.38, P 13.39.

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