Vitamin B_{12} Catalysis of Zinc-Mediated 6-Deoxy-6-iodopyranoside Fragmentation: A Mild and Convenient Preparation of ω-Unsaturated Hexose Derivatives (5-Hexenoses)

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Abstract: The known zinc-mediated preparation of 5-hexenoses by fragmentation of 6-iodopyranosides can be performed in a simple, fast, and mild way, with less side reactions, when vitamin B_{12} is employed as a catalyst.

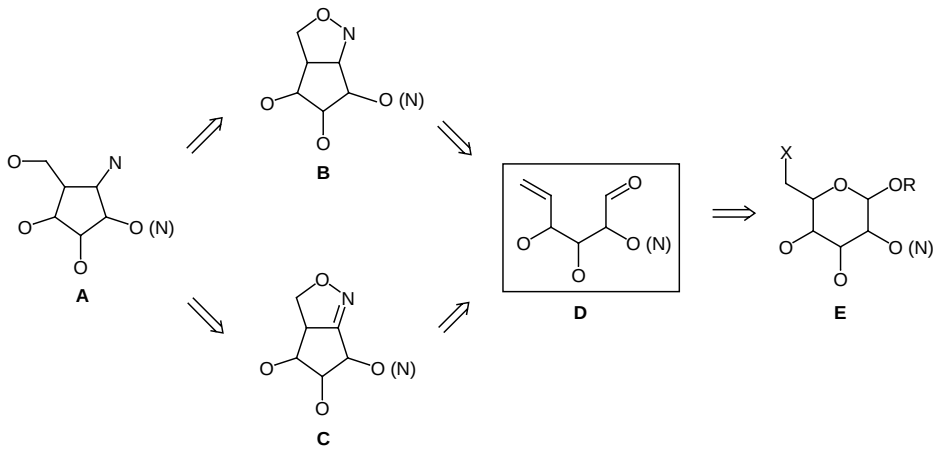
Key words: fragmentation, zinc, vitamin B_{12} catalysis, 6-deoxy-6-iodopyranosides, 5-hexenoses

Unsaturated polyols (enitols) and aminopolyols or hexenose derivatives are versatile intermediates for the synthesis of optically active target compounds.[1] In particular, cyclizations or cycloadditions of such substrates to yield heterocyclic or carbocyclic compounds have found widespread application.[1–7] Starting from hexoses, Bernet and Vasella had shown that transformation to protected 5-hexenoses, via 6-bromo-6-deoxypyranosides, provided straightforward access to one of these classes.[5] The key step, a fragmentation including a reductive elimination (Boord reaction),[8] was effected with zinc or activated zinc in refluxing propanol (93%). The hexenoses were further developed into bicyclic isoxazolidines by dipolar cycloadditions of intermediate nitrones, thus effecting an elegant overall conversion of hexoses into highly functionalized cyclopentane derivatives. This sequence has been useful in many other cases likewise.[1–4,6,9] Since the hexenose products are somewhat unstable and byproducts from further deoxygenation may be formed, a number of other reagents have been proposed for the crucial fragmentation step with such ω-bromo- or ω-iodo compounds. Some of the reagent combinations reported for these or similar cases are zinc-copper pair,[10] zinc activated with $CeCl_3$,[4a,9b] zinc/silver-graphite,[11] or lithium alkyls.[5,8,12] Another combination, zinc with vitamin B_{12} added as a catalyst,[13] had been mentioned in related eliminations for syntheses of long-chain alkenol pheromones[13b] and of tri-*O*-acetylglucal.[13c]

In a project designed to find new structures for glycosidase inhibition, aminocyclopentanepolyols **A** were considered promising candidates,[6,14–16] and respective hexenoses **D** were needed for the preparation of the obvious intermediates, i. e. bicyclic isoxazolidines **B**[6] (vide supra) and related isoxazolines **C**[6a,7,17] (Scheme 1).

6-Bromo-6-deoxypyranosides **E** from the series of the hexose stereoisomers were first taken as starting materials. With the zinc or zinc-copper reagents difficulties were met in several case:[15a,b] In the *gluco* series with tri-*O*-benzyl compounds 2-deoxygenation indeed proved troublesome;[5a,15] in the GlcNAc case and similarly with the galactose bis(acetonide) (vide infra)[16] yields proved difficult to reproduce, and byproducts were found.[18]

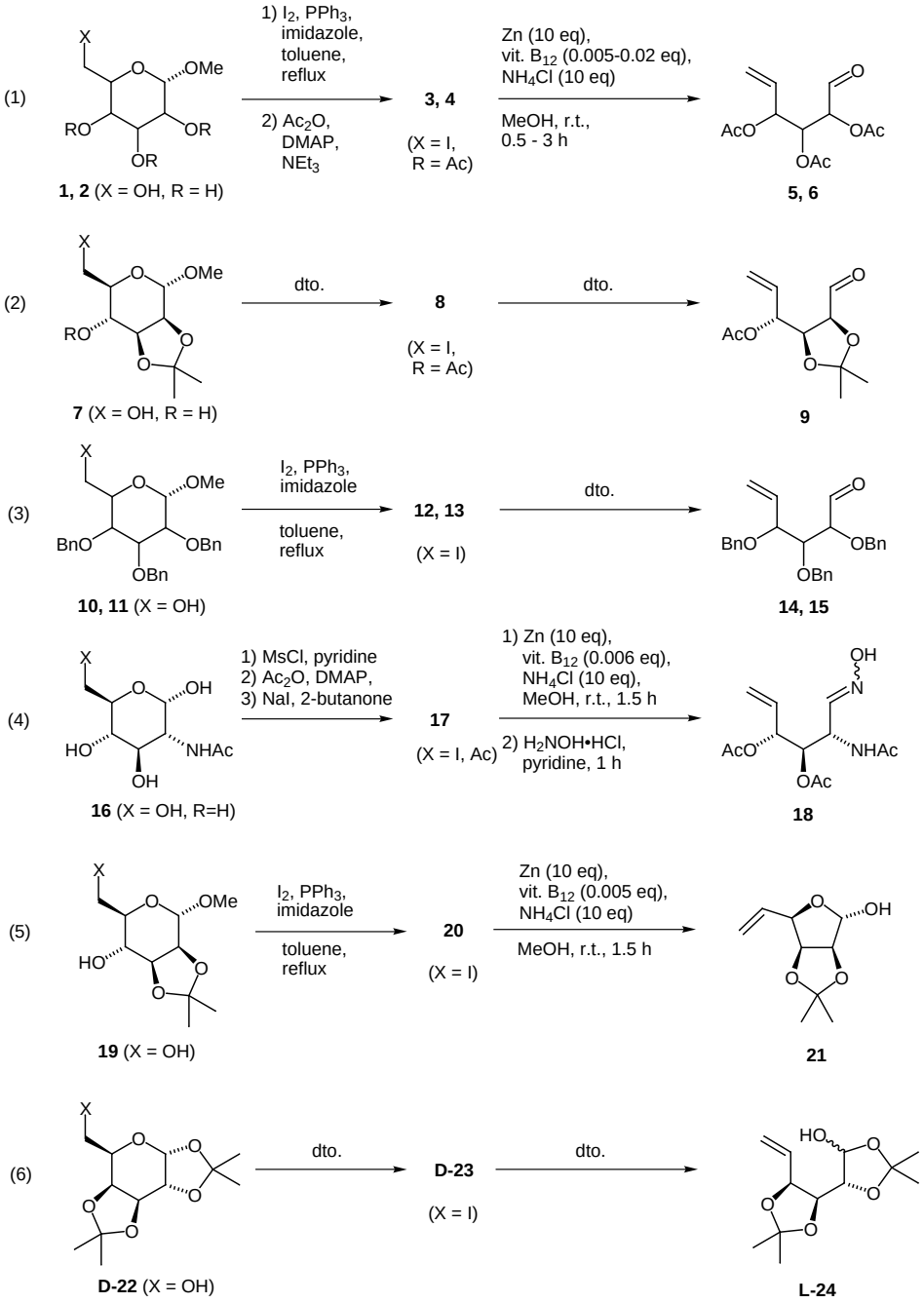
Finally, a new and milder procedure was developed, submitting 6-iodopyranosides to zinc in methanol with 0.5 to 2 mol% of vitamin B_{12} added as a catalyst. In all cases described, the reaction was complete after 3 hours at room



Scheme 1

temperature; it was not necessary to employ activated zinc. Side reactions were not observed, reproducibility was very good, and various *O*-protecting groups could be carried through without trouble, see Equations 1−6 (Scheme 2) and Table 1.

The 6-deoxy-6-iodo compounds **3**, **4**, **8**, **12**, **13**, **20**, and **23** were prepared from the respective protected α-pyranosides **1**, **2**, **7**, **10**, **11**, **19**, and **22**, using the reliable I_2/triphenylphosphane procedure of Garegg and Samuelsson.[19] In the GlcNAc series the iodide **17** was obtained by mesylate substitution, see Equation 4. Upon action of an excess (ca. 10 equiv) of zinc and cyanocobalamin in catalytic amounts, reductive elimination/fragmentation in methanol was complete after 0.5 to 3 hours, as monitored by TLC analyses. From the *gluco*-iodides **3** and **12** with tri-*O*-benzyl and tri-*O*-acetyl protection and the analogous *manno* compounds **4** and **13**, the respective hexenoses **5**, **14**, **6**, and **15** were obtained in good yield and in spectroscopically pure form, albeit with some deviating elemental analyses. For these cases the oximes or other derivatives were prepared and proved satisfactory regarding the latter aspect (see Experimental Part and Table 1). The other *manno* derivative, the 4-*O*-acetyl-2,3-acetonide **8**, was transformed likewise, and the crude product of the



Scheme 2

Table 1 Yields and IR Data of Compounds Prepared

Staring Material, Configuration		Product, Configuration		Yield (%)	Molecular Formula	IR[a] ν (cm^{-1})
3	D-*gluco*	**5**	D-*xylo*	79	$C_{12}H_{16}O_7$ (272.3)	2987 (w), 1750 (br s, C=O), 1422 (m), 1373 (m), 1266 (s), 1217 (s), 1055 (m), 896 (w), 736 (s), 705 (s)
4	D-*manno*	**6**	D-*lyxo*	79[b]	$C_{12}H_{16}O_7$ (272.3)	3055 (m), 2987 (m), 1748 (s, C=O), 1647 (w, C=C), 1422 (m), 1222 (s), 1042 (m), 946 (w), 705 (m)
8	D-*manno*	**9**	D-*lyxo*	96[b]	$C_{11}H_{17}O_5$ (229.2)	2985 (s), 1744 (vs, C=O), 1647 (w, C=C), 1428 (m), 1373 (s), 1234 (s), 1091 (m), 988 (m), 940 (m), 854 (m)
12	D-*gluco*	**14**	D-*xylo*	83[b]	$C_{27}H_{28}O_4$ (416.5)	3054 (s), 2986 (m), 1730 (s, C=O), 1605 (w, C=C), 1451 (s), 1422(m), 1072 (s), 1028 (m), 896 (m)
13	D-*manno*	**15**	D-*lyxo*	75[b]	$C_{27}H_{28}O_4$ (416.5)	2868 (m), 1731 (s, C=O), 1605 (w), 1454 (s), 1330 (w), 1207 (m) 1068 (s), 1028 (s), 933 (m), 736 (s), 698 (s)
17	D-*gluco* (GlcNAc)	**18**	D-*xylo*	92[c]	$C_{12}H_{18}N_2O_6$ (286.3)	3399 (br s, OH, NH), 2935 (m), 1745 (s, C=O), 1664 (m, C=N), 1652 (w, C=C), 1375 (m), 1220 (m), 943 (m)
20	D-*manno*	α-**21**	D-*lyxo*	84[d]	$C_9H_{14}O_4$ (186.2)	3475 (br s, OH), 2943 (s), 1649 (w, C=C), 1379 (s), 1215 (s), 1163 (m), 1072 (m), 944 (s), 879 (s), 853 (s)
D-**23**	D-*galacto*	L-**24**	L-*arabino*	83[b]	$C_{12}H_{20}O_5$ (244.3)	3444 (br s, OH), 2987 (s), 1644 (w, C=C), 1431 (m), 1381 (m), 1212 (s), 1163 (s), 1071 (s), 932 (m)
L-**23**	L-*galacto*	D-**24**	D-*arabino*	55	as above	as above with L-**24**

[a] Recorded as film, except for **21** (KBr).
[b] Satisfactory microanalysis only obtained from derivative, see Experimental Part.
[c] Hexenose not isolated, directly converted to oxime, yield: 92% over 2 steps; IR data from 75:25 *E*/*Z*-mixture of oximes.
[d] α-Furanose form.

hexenose **9** was then converted to the analytically pure nitroaldol product on nitromethane/Bu_4NF•3 H_2O treatment.[20] The sequence was also applied to the *N*-acetylglucosamine derivative **16**, via the iodo compound **17**, which when treated as above led to the stable oxime **18** of the respective D-*xylo*-hexenose in 92% yield.

The mannose-acetonide derivative **20** (from **19**), with free 4-OH, under these conditions led to the α-furanose form of the hexenose **21** (analytically pure), which proved more stable than the other open-chain aldehydes. Finally, the 1,2:3,4-di-*O*-isopropylidenegalactose derivative **22**, via the iodide **23**, on zinc/vitamin B_{12} treatment afforded the bis(acetonide) **24**, with intact hemiacetal moiety. This − presumably labile − structure, not obtainable with the zinc/silver-graphite procedure,[11c] underlines the advantages of the new procedure; actually, the hemiacetal **24** also survived silica gel chromatography as well as Kugelrohr distillation.

The mechanism of such vitamin B_{12}-catalyzed reactions is well understood: Co^{III} of cyanocobalamin with zinc is reduced to Co^{I}, a powerful nucleophile.[13a,21] With alkyl halides or the like, intermediate Co^{III} species are formed that decompose to give an alkene when a leaving group is present in the β-position (cf. reaction modes of coenzyme B_{12}).[13a,21b] It is easy to predict that the ease and mildness of this 6-halopyranoside fragmentation and of selected Boord eliminations using vitamin B_{12} or related cobalt compounds as catalysts will see further applications with sensitive, highly functionalized substrates.

Solvents were purified and dried according to standard procedures. Methy α-D-glucopyranoside, methyl α-D-mannopyranoside, *N*-acetylglucosamine, D-galactose, Ph_3P, I_2, imidazole, Zn (Fluka), and vitamin B_{12} (Aldrich) were purchased and used without further purification. The iodo compounds **3**,[19b] **4**,[19b] **12**,[19c] **17**,[22] **20**,[23] **23**[19b] were prepared according to procedures described in literature. **3**: yield 73%; mp 150−151 °C; $[\alpha]_D^{20}$ +113.0 (*c* = 1.00, $CHCl_3$) {Lit.[19b] mp 151−152 °C; $[\alpha]_D^{20}$ +115.0 (*c* = 1.00, $CHCl_3$)}; **4**: yield 72%; mp 88−90 °C; $[\alpha]_D^{20}$ +48.5 (*c* = 1.00, $CHCl_3$) {Lit.[19b] mp 90−91 °C; $[\alpha]_D^{20}$ +45.0 (*c* = 1.2, $CHCl_3$)}; **12**: yield 84%, mp 68−69 °C; $[\alpha]_D^{20}$ +36.0 (*c* = 1.05, $CHCl_3$) {Lit.[19c] oil; $[\alpha]_D^{20}$ +61.0 (*c* = 1, EtOAc)}; **17**: yield 75%; mp 204 °C (dec.); $[\alpha]_D^{20}$ +86.0 (*c* = 0.96, $CHCl_3$) {Lit.[22] mp 196−197 °C (dec.); $[\alpha]_D^{20}$ +92.2 (*c* = 1.2, $CHCl_3$)}; **20**: yield 86%; mp 110−111 °C; $[\alpha]_D^{20}$ +45.7 (*c* = 1.10, $CHCl_3$) {Lit.[23] mp 111−112 °C; $[\alpha]_D^{20}$ +46.0 (*c* = 1.3, $CHCl_3$)}; **23**: yield 82%; mp 59−60 °C; $[\alpha]_D^{20}$ − 48.0 (*c* = 1.16, $CHCl_3$) {Lit.[19b] mp 58 °C; $[\alpha]_D^{20}$−49.0 (*c* = 1.00, $CHCl_3$)}.

TLC was performed on silica F_{254}-coated aluminum sheets (E. Merck) using mixtures of EtOAc/petroleum ether (bp 40−70 °C) and propan-2-ol/petroleum ether, with detection by UV at 254 nm or by heating with a solution of cerium(IV) sulfate (1 g), ammonium molybdate (2.1 g), and concd H_2SO_4 (31 mL) in H_2O (500 mL).[24] Silica gel (Merck, 32−63 μm) was used for chromatography. MPLC was done using a Lewa pump with a column (4 cm × 40 cm) packed with LiChroprep Si 60 (15−25 μm, Merck, ca. 11500 theoretical plates),[25] detection by a UV/VIS spectrometer 97.00 (Knauer). Mps were determined on a Fisher-Johns apparatus and are uncorrected. The optical rotations were measured on a Perkin-Elmer 241 MC polarimeter using the Drude method to calculate $[\alpha]_D$ from the values found at 546 and 579 nm. IR spectra were recorded on a Bruker IFS

28 spectrometer. NMR spectra were obtained from Bruker AC 250, ARX 300 and ARX 500 spectrometers (^{1}H: 250.1, 300.1, or 500.1 MHz, ^{13}C: 62.9, 75.5, or 125.8 MHz) with TMS as internal standard; evaluation of ^{1}H NMR spectra according to 1st order interpretation; multiplicity of ^{13}C NMR signals from broad-band decoupled or DEPT spectra. The NMR data of compounds **5, 6, 9, 14, 15, 18, 21** and **24** prepared are shown in Tables 2 and 3.

Methyl 4-*O*-Acetyl-6-deoxy-6-iodo-2,3-*O*-isopropylidene-α-D-mannopyranoside (8)

According to Ref.,[19] isopropylidenemannopyranoside **7** (2.75 g, 8.00 mmol) and DMAP (20 mg) were dissolved in Et_3N (4.00 g) and cooled to 0 °C. Within 20 sec Ac_2O (1. 02 g, 10.00 mmol) was added dropwise. After 30 min the ice-bath was removed and the yellowish solution stirred for another 4 h at r.t. Evaporation of volatiles and filtration over silica gel (40 g, petroleum ether/EtOAc, 70:30) afforded 3.09 g (99%) of a colorless oil, which crystallized at −30 °C; mp 39−40 °C; $[\alpha]_D^{20}$ +25.2 (*c* = 0.63, $CHCl_3$).

$C_{12}H_{19}IO_6$	calc.	C	37.32	H	4.96	I	32.86
(386.2)	found		37.18		4.92		32.64

Methyl 2,3,4-Tri-*O*-benzyl-6-deoxy-6-iodo-α-D-mannopyranoside (13)

According to Ref.[19] to a stirred solution of methyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside[5b] (4.50 g, 9.69 mmol) in toluene (100 mL) at 80 °C was added I_2 (3.60 g, 14.2 mmol), Ph_3P (7.30 g, 27.8 mmol), and imidazole (3.80 g, 55.8 mmol) and then kept at 80 °C for 4 h. The solvent was removed by evaporation and the resulting oil purified by column chromatography (silica gel, 150 g, petroleum ether/EtOAc, 90:10 → 80:20) to yield 4.77 g (86%) of a colorless oil; $[\alpha]_D^{20}$ +22 (*c* = 0.95, $CHCl_3$).

$C_{28}H_{31}IO_5$	calc.	C	58.49	H	5.43	I	22.07
(575.0)	found		58.27		5.38		21.85

5,6-Dideoxy-2,3-*O*-isopropylidene-α-D-*lyxo*-5-hexenofuranose (21); Typical Procedure

To a stirred suspension of Zn (916 mg, 14.0 mmol) and NH_4Cl (750 mg, 14.0 mmol) in MeOH (20 mL) a catalytic amount of vitamin B_{12} (5 mg, 0.006 mmol) was added at r.t. After 10 min, a solution of **20** (480 mg, 1.40 mmol) in MeOH (2 mL) was added. The resulting suspension was stirred for 90 min at r.t. Undissolved material was filtered off and washed with MeOH. The filtrate was

Table 2 ^{1}H NMR Data Hexenoses Prepared ($CDCl_3$/TMS)

Compound	Chemical Shifts δ (ppm)							
	1-H	2-H	3-H	4-H	5-H	6-H_E	6-H_Z	Others
5	9.49	5.28	5.53[a]	5.54[a]	5.77	5.35	5.38	2.06, 2.10, 2.22 (3 $COCH_3$)
6	9.48	5.24	5.47	5.63	5.74	5.35	5.43	2.09, 2.09, 2.20 (3 $COCH_3$)
9	9.67	4.42	4.52	5.33	5.87	5.33	5.38	1.42, 1.63 [$C(CH_3)_2$], 2.09 ($COCH_3$)
14	9.64	3.87	3.79	4.15	5.82	5.24	5.27	4.35, 4.47, 4.53, 4.57, 4.70, 4.71 (3 CH_2Ph), 7.15−7.42 (C_6H_5)
15	9.65	-[b]	3.89	-[b]	5.85	5.34	5.37	4.31−4.76 (m, 2-H, 4-H, 3 CH_2Ph), 7.15−7.45 (C_6H_5)
18[c]	7.42	5.02	5.29	5.49	5.80	5.30	5.34	2.04, 2.08, 2.10 (3 $COCH_3$), 6.75 (NH), 9.55 (OH)
α-**21**	5.41	4.64	4.73	4.62	5.99	5.34	5.42	1.32, 1.47 [$C(CH_3)_2$], 3.00 (OH)
α-L-**24**[d]	5.40	4.01	4.48	4.69	6.02	5.29	5.40	1.38, 1.42, 1.57, 1.58 [2 $C(CH_3)_2$], 3.61 (OH)
β-L-**24**[d]	5.39	3.99	4.20	4.66	5.94	5.33	5.40	1.40, 1.49, 1.52, 1.55 [2 $C(CH_3)_2$], 3.61 (OH)

Compound	Coupling Constants *J* (Hz)							
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6E}$	$J_{5,6Z}$	$J_{6E,6Z}$	Others
5	~0	1.6	1.3	6.5	10.4	17.1	1.8	$J_{4,6E} = J_{4,6Z} = 0.9$
6	0.7	5.2	5.4	6.4	10.4	17.0	1.2	$J_{4,6E} = J_{4,6Z} = 0.9$
9	2.3	7.7	3.8	6.8	10.5	17.3	1.8	$J_{4,6E} = J_{4,6Z} = 1.0$
14	1.0	4.4	5.0	7.7	11.6	16.0	1.8	$J_{4,6E} = J_{4,6Z} = 0.9$, $J_{CH_2\ Ph} = 11.6$ (3 ×)
15	1.5	5.6	3.7	7.8	10.3	17.5	1.8	$J_{4,6E} = J_{4,6Z} = 1.0$
18[c]	4.0	4.5	5.5	5.9	10.4	16.8	-[b]	$J_{2,NH} = 9.0$
α-**21**	~0	5.8	3.7	7.4	10.4	17.5	1.7	$J_{4,6E} = 0.8$, $J_{4,6Z} = 1.0$, $J_{1,OH} = 2.3$
α-L-**24**[d]	3.9	6.3	6.6	8.2	10.1	17.1	1.6	$J_{4,6E} = J_{4,6Z} = 0.9$
β-L-**24**[d]	3.6	5.1	6.8	8.2	10.2	17.1	1.6	$J_{4,6E} = J_{4,6Z} = 0.9$

[a] Assignments may be reversed.[b] Not identified due to overlapping signals.
[c] ^{1}H NMR Data from (*E*)-oxime; from the (*Z*)-isomer only few data were identified due to overlapping signals [*E*/*Z*-mixture = 75:25]: 6.28 ($J_{2,NH}$ = 6.3 Hz, NH), 6.62 ($J_{1,2}$ = 5.7 Hz, 1-H), 10.23 (br s, OH), see Experimental.
[d] Data obtained from a 40:60-mixture of α/β-anomers; signals for 6-H_Z and OH coinciding.

Table 3 ^{13}C NMR Chemical Shifts of Hexenoses Prepared, δ[a] (ppm)

Compound	C-1	C-2	C-3	C-4	C-5	C-6	Others
5	193.8	70.3[b]	72.4[b]	75.5[b]	130.9	120.4	20.1, 20.2, 20.5 (3 $COCH_3$), 169.1, 169.3, 169.5 (3 $COCH_3$)
6	195.1	71.1[b]	71.6[b]	75.4[b]	131.2	120.4	20.2, 20.4, 20.6 (3 $COCH_3$), 169.3, 169.5, 169.7 (3 $COCH_3$)
9	200.0	79.9[b]	80.3[b]	71.3	132.0	119.6	24.9, 26.5 [$C(CH_3)_2$], 111.0 [$C(CH_3)_2$], 20.9 ($COCH_3$), 169.1 ($COCH_3$)
14	201.4	79.8	81.3	82.2	134.6	119.3	70.8, 73.1, 74.3(3 OCH_2Ph), 127.1 - 128.4 (3*o*-, *m*-, *p*-C_6H_5), 137.1, 137.5, 137.7 (3 *i*-C_6H_5)
15	201.7	80.5[b]	82.8[b]	83.6[b]	135.1	119.9	70.7, 72.7, 74.1(3 OCH_2Ph), 127.6 - 128.5 (3*o*-, *m*-, *p*-C_6H_5), 137.3, 137.8, 138.0 (3 *i*-C_6H_5)
(*E*)-**18**[c]	147.1	48.8	72.2[b]	72.5[b]	131.6	119.7	20.6, 21.0, 22.9 (3 $COCH_3$), 170.1, 170.4, 170.6 (3 $COCH_3$)
(*Z*)-**18**[c]	147.0	50.5	72.7[b]	73.0[b]	131.5	120.1	20.7, 21.0, 23.1 (3 $COCH_3$), 170.2, 170.3, 170.9 (3 $COCH_3$)
α-**21**	101.1	81.5	81.5	85.8	132.1	119.3	24.9, 26.1 [$C(CH_3)_2$], 112.7 [$C(CH_3)_2$]
α-L-**24**[d]	97.3	82.1	77.3[b]	78.9[b]	134.1	120.0	26.9, 27.1, 27.5, 28.6 [2 $C(CH_3)_2$], 110.5, 111.1 [2 $C(CH_3)_2$]
β-L-**24**[d]	95.0	77.3[b]	78.2[b]	78.5[b]	133.7	119.1	25.4, 25.4, 26.2, 27.4 [2 $C(CH_3)_2$], 109.4, 109.6 [2 $C(CH_3)_2$]

[a] Recorded in $CDCl_3$.
[b] Assignments may be reversed.
[c] From 75:25-mixture of *Z*/*E*-oximes, see Experimental.
[d] Data received from a 40:60-mixture of α/β-anomers.

evaporated, the reddish residue dissolved in EtOAc (20 mL), washed with a mixture of H_2O and brine (5 mL each), the organic layer re-extracted with EtOAc (3 × 10 mL) and then the combined organic layers were dried (Na_2SO_4). Evaporation afforded the crude product **21** as a yellowish oil. For correct elemental analysis purification of this by filtration over silica gel (20 g, eluent Et_2O) gave a pale yellow oil (**21**, 233 mg, 90%). Further purification by MPLC (petroleum ether/propan-2-ol, 95:5, 210 nm) afforded **21** as a colorless oil (218 mg, 84%), which crystallized at −30 °C; mp 55−56 °C; $[\alpha]_D^{20}$ −29.0 (*c* = 0.57, $CHCl_3$).

$C_9H_{14}O_4$	calc.	C 58.05	H 7.58		
(186.2)	found	57.92	7.61		

2,3,4-Tri-*O*-acetyl-5,6-dideoxy-D-*xylo*-5-hexenose (5)
From **3** (1g, 2.32 mmol) following the Typical Procedure; purification by chromatography (eluent petroleum ether/EtOAc, 90:10 → 70:30), yield: 502 mg (79%); colorless oil; $[\alpha]_D^{20}$ −20.4 (*c* = 1.22, $CHCl_3$) {Lit.[11d] $[\alpha]_D^{20}$ +3.9 (*c* = 13.3, CH_2Cl_2); no analysis given}.

$C_{12}H_{16}O_7$	calc.	C 52.95	H 5.92		
(272.3)	found	52.75	6.04		

2,3,4-Tri-*O*-acetyl-5,6-dideoxy-D-*lyxo*-5-hexenose (6)
Prepared from **4** (400 mg, 0.93 mmol) according to the Typical Procedure; yield: 220 mg (79%), colorless oil; $[\alpha]_D^{20}$ +41.2 (*c* = 0.92, $CHCl_3$), spectroscopically pure, but incorrect elemental analysis.

Isoxazolidine derivative with MeNHOH: 63%;[16b] colourless oil; $[\alpha]_D^{20}$ −75.0 (*c* = 1.33, $CHCl_3$).

$C_{13}H_{19}NO_7$	calc.	C 51.82	H 6.36	N 4.66		
(301.3)	found	51.80	6.50	4.58		

4-*O*-Acetyl-5,6-dideoxy-2,3-*O*-isopropylidene-D-*lyxo*-5-hexenose (9)
Following the Typical Procedure; from **8** (3.09 g, 8.00 mmol), yield of **9**: 1.77 g (96%); colorless oil; $[\alpha]_D^{20}$ −44.2 (*c* = 0.53, $CHCl_3$); spectroscopically pure, deviating elemental analysis.

Nitromethane adduct (with $Bu_4NF•3H_2O$); colorless oil; yield: 64%;[20] dr = 90:10; $[\alpha]_D^{20}$ −22.0 (*c* = 0.40, $CHCl_3$).

$C_{12}H_{19}NO_7$	calc.	C 49.82	H 6.62	N 4.84		
(289.3)	found	49.61	6.74	4.53		

2,3,4-Tri-*O*-benzyl-5,6-dideoxy-D-*xylo*-5-hexenose (14)
From **12** (6.00 g, 10.7 mmol) according to the Typical Procedure; yield: **14** 3.73 g (83%); colorless oil; $[\alpha]_D^{20}$ −15.2 (*c* = 1.05, $CHCl_3$); spectroscopically pure, deviating elemental analysis.

Oxime derivative: yield 75%; *E*/*Z* = 67:33; mp 60-62 °C; $[\alpha]_D^{20}$ +20.0 (*c* = 1.01, $CHCl_3$).

$C_{27}H_{29}NO_4$	calc.	C 75.17	H 6.77	N 3.24		
(431.5)	found	75.28	6.86	3.22		

2,3,4-Tri-*O*-benzyl-5,6-dideoxy-D-*lyxo*-5-hexenose (15)
According to the Typical Procedure; from **13** (575 mg, 1.00 mmol), yield: **15** 312 mg (75%); colorless oil; $[\alpha]_D^{20}$ −9.5 (*c* = 1.21, $CHCl_3$); spectroscopically pure, deviating elemental analysis.

Oxime derivative: colorless oil, yield 69%; *E*/*Z* = 75:25; $[\alpha]_D^{20}$ −11.0 (*c* = 1.05, MeOH).

$C_{27}H_{29}NO_4$	calc.	C 75.16	H 6.77	N 3.25		
(431.5)	found	75.09	6.83	3.24		

2-Acetamido-3,4-di-*O*-acetyl-2,5,6-trideoxy-D-*xylo*-5-hexenose oxime (18)
To a solution of vitamin B_{12} (20 mg, 15 μmol) in MeOH (50 mL) was added Zn (2.60 g, 26.9 mmol) and NH_4Cl (2.14 g, 26.9 mmol). After the mixture had become green, **17** (1.23 g, 2.69 mmol) was added and the suspension stirred at r.t. for 90 min. Then pyridine (2 mL) and $H_2NOH•HCl$ (374 mg, 5.38 mmol) were added. After stirring for another 90 min the solids were filtered off and the solution was evaporated. The residue then was purified by chromatography (CH_2Cl_2/MeOH, 97:3) to give 710 mg (92%) of the oxime **18;** colorless, analytically pure oil; *E*/*Z* = 75:25.

(*E*)-Isomer from repeated chromatography as above; mp 139-140 °C, $[\alpha]_D^{20}$ −2.5 (*c* = 1.05, $CHCl_3$).

$C_{12}H_{18}N_2O_5$	calc.	C 50.34	H 6.34	N 9.78		
(286.3)	found	50.07	6.41	9.26		

5,6-Dideoxy-1,2:3,4-di-*O*-isopropylidene-L-*arabino*-5-hexenose (L-24)

According to the Typical Procedure; D-**23** (3.58 g, 9.6 mmol) gave 1.95 g (83%) of L-**24**, colourless oil; anomer ratio α:β = 33:67; $[\alpha]_D^{20}$ +15.0 (*c* = 1.08, $CHCl_3$), spectroscopically pure, deviating elemental analysis.

Corresponding oxime: colorless oil; yield 95%; *E*/*Z* = 81:19; $[\alpha]_D^{20}$ −24.0 (*c* = 1.06, $CHCl_3$).

$C_9H_{15}NO_4$	calc.	C	53.72	H	7.51	N	6.96
(201.2)	found		53.59		7.61		6.97

5,6-Dideoxy-1,2:3,4-di-*O*-isopropylidene-D-*arabino*-5-hexenose (D-24)

As described for L-**24**, starting from L-galactose via L-**22** and L-**23** (659 mg, 1.8 mmol); D-**24**: 240 mg (55%); colorless, analytically pure oil after purification by chromatography with petroleum ether/EtOAc (1:1), anomer ratio α:β = 41:59; $[\alpha]_D^{20}$ −20.0 (*c* = 0.96, $CHCl_3$).

$C_{12}H_{20}O_5$	calc.	C	59.00	H	8.25
(244.3)	found		58.66		8.30

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