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RING EXPANSIONS IN CARBOHYDRATE CHEMISTRY: *gem*-AZOACETATES*

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ABSTRACT

On treatment with lead tetraacetate, blocked furanos-3-ulose and furanos-3-uloside *p*-nitrophenylhydrazones afforded the corresponding "*gem*-azoacetates". The reaction was not stereospecific, except when the starting hydrazone was blocked by a 1,2-*O*-isopropylidene group. Upon deacetylation of the former compounds, *gem*-azoalcohols of various stabilities were formed. They rearranged, either on silica gel or upon alkaline treatment, leading regiospecifically to ring-expanded 3-azapyranosic *N*-arylaminolactams. This regiospecific ring-enlargement reaction, which maintains the stereochemistry of every asymmetric carbon atom of the molecule and breaks the carbon chain of the starting ketose, constitutes a useful source of chirons of various sizes. In the pyranose series, the reaction was not regiospecific, affording a mixture.

INTRODUCTION

Ever since the classical work of Emil Fischer[1], hydrazines have been favorite reagents amongst carbohydrate chemists: Freudenberg[2] synthesized deoxy hydrazino sugars; H. O. L. Fischer[3], formazans; and Helferich[4], several *N*-acylhydrazones.

By lead tetraacetate oxidation of sugar hydrazones, we prepared[5,6] a novel series of nitrogen-bearing sugars, "*gem*-azoacetates", *e.g.*, **1** and **4**, from which unexpectedly stable arylazo sugars, *e.g.*, **2** and **5**, were obtained. On treatment with base, **2** and **5** rearranged to the ring-expanded *N*-arylaminolactams **3** and **6**, respectively, **7** being prepared by acetylation of **6**.

In all series studied so far, the ketose *p*-nitrophenylhydrazones gave, stereo-

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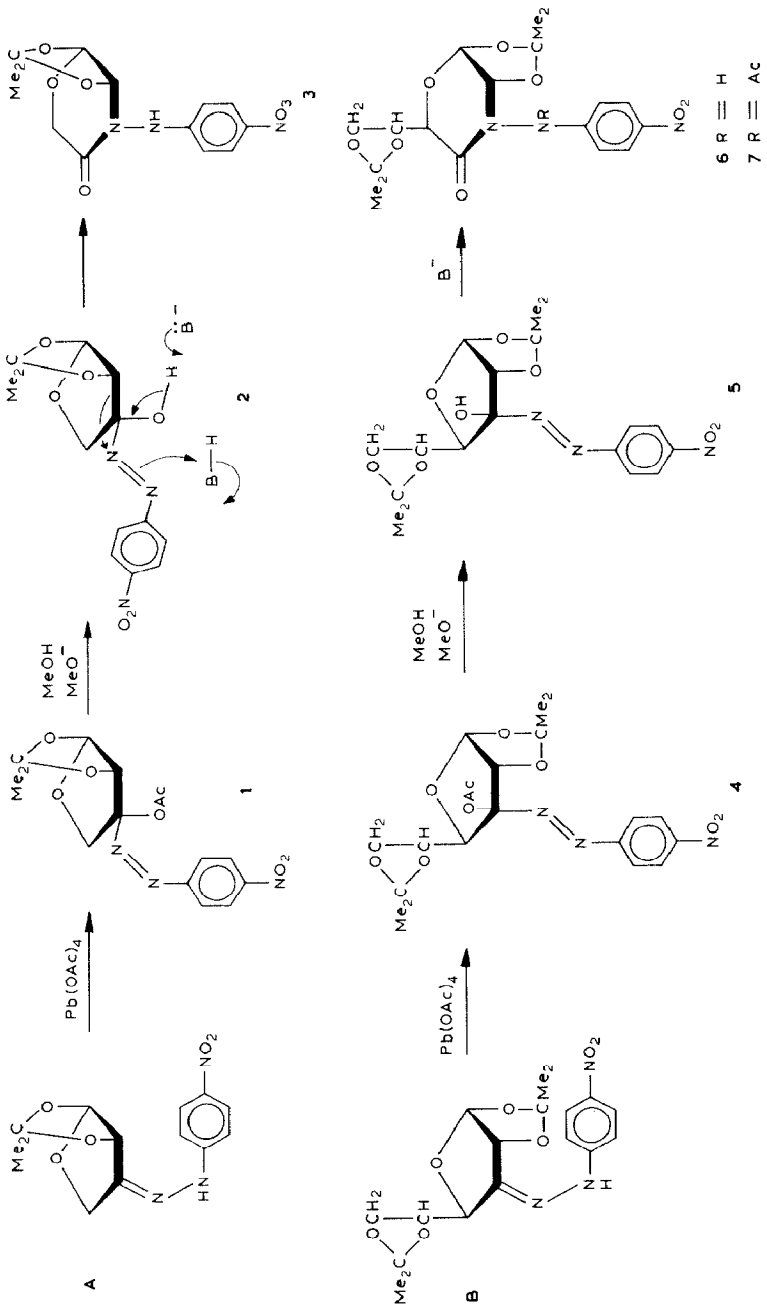
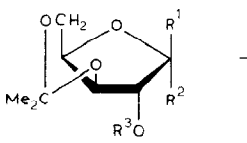

Pb(OAc)4
MeOH
MeO⁻
A
1
2
3
B
4
5
6 R = H
7 R = Ac

specifically, one *gem*-azoacetate which rearranged regiospecifically to the *N*-aminolactam by breaking the C–C bond closer to the anomeric carbon atom. To investigate the scope of the reaction and particularly the influence of the neighboring isopropylidene group common to the compounds previously studied we prepared, as new models for this reaction, a series of 3-ketofuranoside *p*-nitrophenylhydrazones derivatives devoid of this blocking group and having different configurations, as well as a pyranos-4-uloside *p*-nitrophenylhydrazone. Compounds[6] **1, 2** and **4, 5** have been used for comparative ^{1}H-n.m.r. and circular dichroism studies. Properties of compounds **3, 6,** and **7** which have been preliminarily described[5] will be fully reported here.

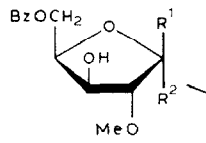
RESULTS AND DISCUSSION

Etherification of O-2 of methyl 3,5-*O*-isopropylidene-α- and -β-D-xylofuranoside[7] with methyl iodide or benzyl chloride afforded compounds **8–11**, which were hydrolyzed to the corresponding *O*-deisopropylidenated compounds; these were not isolated, except for the crystalline **12**, but submitted either to selective benzoylation[8], leading to **13** and **14** from **8** and **9**, respectively, or to benzylidenation according to Evans[9], affording the known[10] **15** and **16**. Hydrogenolysis of the latter two compounds led to **17** and **18**, whose characteristics have been reported by Lipták *et al.*[10], except for the ^{1}H-n.m.r. spectrum of the β anomer **17**. Compounds **13** and **14** were oxidized (chromic oxide, pyridine[11]) to the corresponding furanosiduloses **19** and **20, 20** being converted into the *p*-nitrophenylhydrazone **21**. On the other hand, **17** and **18** were oxidized (catalytic ruthenium tetraoxide[12]) to **22** and **23**, which led to the corresponding *p*-nitrophenylhydrazones **24** and **25**, respectively. The *p*-nitrophenylhydrazones were generally obtained as mixtures of the *Z* and *E* isomers, as determined by ^{1}H-n.m.r. spectroscopy[13]. On lead tetraacetate oxidation, the hydrazones **21, 24,** and **25** gave a mixture of epimeric *gem*-azoacetates, respectively **26** and **27, 28** and **29,** and **30** and **31**. This contrasted with the stereospecificity observed in the previous series[5,6], where the reaction was applied to compounds bearing an *O*-isopropylidene group α to the hydrazono group. Azoacetates **26, 27, 28, 29,** and **31** were relatively stable compounds, but it was impossible to eliminate the last traces of solvent from syrupy **30** without decomposition of this compound. Whereas azoalcohols from previous series (*e.g.*, **2, 5,** and **C**) were stable compounds, deacetylation of **28–31** afforded very unstable *gem*-azoalcohols (**32–35**, respectively) which could only be characterized by n.m.r. spectroscopy. Some ^{1}H-n.m.r. data of compounds **1, 2, 4, 5,** and **26–35** are collected in Table I.

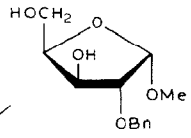
The configuration of C-3 of molecules **1, 2, 4,** and **5** had been established[6] by comparing the effect of deacetylation on the chemical shifts of H-2 and H-4. For the more-flexible molecules **26–35**, the configurational assignments are not so straightforward. Compounds **26–35** constitute five pairs of isomers, each azoalcohol being synthetically correlated to its corresponding azoacetate. The rotatory power



8 $R^1 = OMe, R^2 = H, R^3 = Me$
9 $R^1 = H, R^2 = OMe, R^3 = Me$
10 $R^1 = OMe, R^2 = H, R^3 = Bn$
11 $R^1 = H, R^2 = OMe, R^3 = Bn$



13 $R^1 = OMe, R^2 = H$
14 $R^1 = H, R^2 = OMe$



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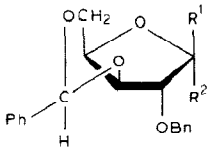
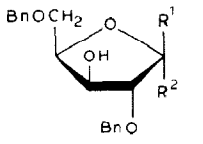
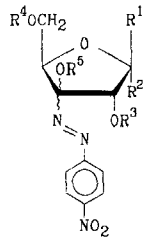


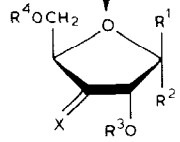
15 $R^1 = OMe, R^2 = H$
16 $R^1 = H, R^2 = OMe$



17 $R^1 = OMe, R^2 = H$
18 $R^1 = H, R^2 = OMe$



26, 27 $R^1 = H, R^2 = OMe, R^3 = Me, R^4 = Bz, R^5 = Ac$
28, 29 $R^1 = OMe, R^2 = H, R^3 = R^4 = Bn, R^5 = Ac$
30, 31 $R^1 = H, R^2 = OMe, R^3 = R^4 = Bn, R^5 = Ac$
32, 33 $R^1 = OMe, R^2 = H, R^3 = R^4 = Bn, R^5 = H$
34, 35 $R^1 = H, R^2 = OMe, R^3 = R^4 = Bn, R^5 = H$



19 $R^1 = OMe, R^2 = H, R^3 = Me, R^4 = Bz, X = O$
20 $R^1 = H, R^2 = OMe, R^3 = Me, R^4 = Bz, X = O$
21 $R^1 = H, R^2 = OMe, R^3 = Me, R^4 = Bz, X = NNHC_6H_4NO_2\text{-}p$
22 $R^1 = OMe, R^2 = H, R^3 = R^4 = Bn, X = O$
23 $R^1 = H, R^2 = OMe, R^3 = R^4 = Bn, X = O$
24 $R^1 = OMe, R^2 = H, R^3 = R^4 = Bn, X = NNHC_6H_4NO_2\text{-}p$
25 $R^1 = H, R^2 = OMe, R^3 = R^4 = Bn, X = NNHC_6H_4NO_2\text{-}p$

TABLE I

^{1}H-N.M.R. DATA FOR AZOALCOHOLS AND AZOACETATES

Compound	*Chemical shifts (p.p.m.)*				*Coupling constants (Hz)*		*Configuration*
	H-1	*H-2*	*H-4* endo	*H-4* exo	$J_{1,2}$	$J_{4,5}$	
1	6.12	4.93	4.92	4.45	3.8		β-D-*threo*
2	6.24	4.54	4.96	3.94	3.8		β-D-*threo*
4	6.03	5.38	4.88		3.6	6.3	α-D-*gluco*
5	6.06	4.39	4.97		3.2	7.9	α-D-*gluco*
26	5.37	4.42	4.95		4.5	7.0–3.9	α-D-*xylo*
27	5.32	4.52	5.31		4.9	4.1–4.0	α-D-*ribo*
28	5.22	4.61	4.78		2.0	7.0–3.5	β-D-*xylo*
32	5.27	4.40	4.50		4.8	5.9	β-D-*xylo*
29	5.19	4.70	5.02		4.0	4.5	β-D-*ribo*
33	5.40	4.36	4.65		3.8	5.0	β-D-*ribo*
30	5.21	4.52	4.82		4.8	8.2–2.8	α-D-*xylo*
34	5.11	4.31	4.60		4.8	6.0–6.5	α-D-*xylo*
31	5.07	4.74	5.11		5.0	3.5–3.5	α-D-*ribo*
35	5.06	4.23	4.66		4.8	5.5	α-D-*ribo*

TABLE II

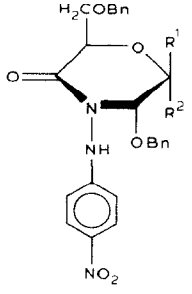
CHIROPTICAL DATA FOR AZOACETATES (IN ETHANOL)

Compound	$[\alpha]_D$ *(degrees)*	*C.d. data*			*Configuration*
4	+376.5	228 (+16500)	276 (+44000)	403 (−3670)	*xylo*
26	+131	238 (−5100)	279 (+20400)	394 (−4000)	*xylo*
27	+13	243 (+4700)	280 (−1600)	392 (−3000)	*ribo*
28	+40.3	247 (−7100)	285 (+12500)	~370 (−?)	*xylo*
29	−55.2	~220 (+?)	272 (−30000)	386 (−?)	*ribo*
30	~+105	288 (−3000)	276 (+16200)	385 (−2140)	*xylo*
31	−62	241 (+3140)	282 (−10700)	394 (−5300)	*ribo*

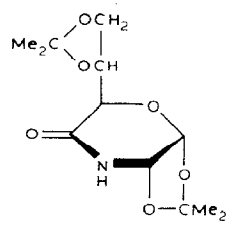
of the azoacetates was shown (see Table II) to be more affected by an inversion at C-3 [differences between epimers (anomers) at C-3 ranging from 95 to 167°] than by any other configurational change. On this basis, these compounds could be sorted into two configurationally homogeneous subsets, **A** (compounds **26, 28, 30, 32,** and **34**) and **B** (**27, 29, 31, 33,** and **35**). This view was confirmed by the ^{1}H-n.m.r. data (see later) and by the c.d. spectra of the azoacetates, in which a band at ~280 nm, associated with the 3-acetoxyl group (as it did not exist for such compounds lacking this group as *gem*-azoalcohols **2** and **5**) presented a positive ellipticity for azoacetates **26, 28,** and **30**, and a negative one for **27, 29,** and **31**. Under these conditions, determination of the configuration of any one of the azoacetates was sufficient to establish the structures of all of these compounds. Compound **26** was

the only crystalline azoacetate (fine yellow needles, cross-section <0.01 mm^2, crystal system orthorhombic, space group $P2_12_12_1$, a = 6.369(1), b = 15.455(2), c = 24.112(5) Å, V = 2373.4 Å^3, μ = 0.094 mm^{-1} (MoKα), d_c = 1.258 g.cm^{-3}, Fooo = 944). Several crystals were measured, but all attempts to solve the structure (MULTAN 84[14]) did not lead to any useful result. The diffraction measurements showed that the relative values of diffracted intensities varied from one crystal to another, whereas the cell parameters remained constant. Moreover, the diffracted intensities decreased strongly with the Bragg angle [~600 observed reflexions with $Fo > 3\sigma(Fo)$ for 1500 measured reflexions]. It was concluded from these observations that the structure was certainly disordered, and that several conformations, in variable proportions from one crystal to another, were present in the crystal.

A direct proof of the structure being unavailable, we had to resort to indirect ones. In a related series[15], methyl 3,5-*O*-isopropylidene-2-(*p*-nitrophenylazo)-β-D-xylofuranoside, whose (2*R*) configuration had been proved by X-ray diffraction, presented in its c.d. spectra a band of negative ellipticity at 270 nm, indicating a 3(*S*) configuration for compounds of the subset **A**. The n.m.r. data (see Table I) were also in favor of a D-*xylo* configuration for subset **A** on the following bases. Examination of molecular models showed that δ-H-4 should be globally more affected by the acetoxyl group in the *ribo* than in the *xylo* series. As H-4 of the



36 R^1 = OMe, R^2 = H
37 R^1 = H, R^2 = OMe



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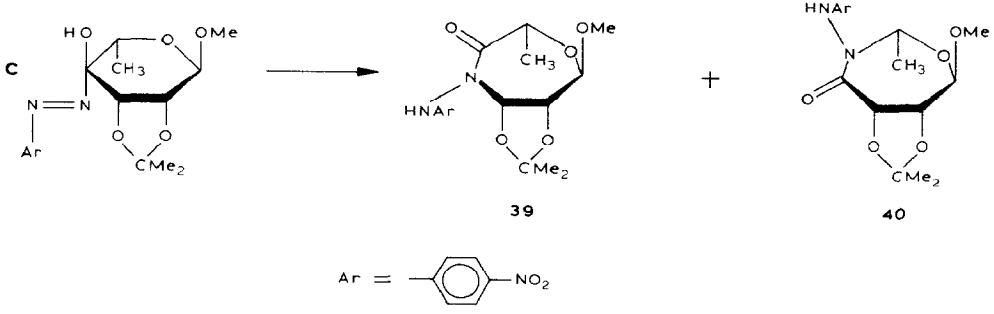

39

40

Ar =

TABLE III

N.M.R. DATA FOR *N*-ARYLAMINOLACTAMS

Compound	*^{1}H-N.m.r. data*								*^{13}C-N.m.r. data*				
	Chemical shifts (p.p.m.)						*Coupling constants (Hz)*		*Chemical shifts (p.p.m.)*				
	H-1	*H-2*	*H-5*	*H-6*	*Ph*	*NH*	$J_{1,2}$	$J_{5,6}$	*C-1*	*C-2*	*C-4 (C=O)*	*C-5*	*C-6*
3	5.86	5.50	4.42 4.26		8.03–8.13 6.78–6.88	7.01	4.9		96.49	87.58	169.94	61.93	
6	5.94	5.51	4.57	4.68	8.02–8.18 6.76–6.91	6.93	5.0	3.6	96.0	87.6	169.8	74.8	70.80
7a	5.87	5.56	4.52	4.63–4.82	8.15–8.25 7.64–7.74		4.9	3.9					
7b	5.79	5.36	4.59	4.63–4.82	8.13–8.23 7.44–7.54		4.9						
36	4.90	4.85	4.65	3.92	7.95–8.05 6.78–6.90	6.93	2.5	5.0	99.34	89.33	167.73	74.65	71.00
37	5.15	4.91	4.53	3.93	7.80–7.92 6.60–6.70	6.38	3	2.0 3.0	96.98	85.95	167.79	73.97	71.23
38	5.72	5.37	4.44	4.73		6.55	5.0 $J_{2,NH}$ = 5 Hz	4.1	94.72	79.77	171.87	73.87	69.39

azoacetates of the **A** subset was always more deshielded than the corresponding proton of the **B** subset, and moreover, the upfield shift of H-4 when going from the azoacetate to the azoalcohol was larger for the **A** subset than for the **B**, the attribution of the *xylo* configuration for the **A** subset was confirmed.

The *N*-arylaminolactams **3** and **6** were obtained on treatment of tetrahydrofuran solutions of the stable azoalcohols **2** and **5** with potassium *tert*-butoxide. Under the same conditions, **32** and **33** afforded **36** in 30% yield, whereas the α-isomers **34** and **35** were entirely decomposed. In the last two series, the azoalcohols, as well as the corresponding arylaminolactams, were decomposed by the *tert*-butoxide anion. In fact, milder conditions gave, in some cases, better results than alkaline treatment. For example, **37** was obtained in a very good yield upon attempted chromatographic separation of **34** from **35**, and ^{1}H- and ^{13}C-n.m.r. reinvestigation of crystalline samples of **2** and **5** that had been kept for several years at 4° showed that **5** had remained unchanged, whereas **2** had spontaneously rearranged to the *N*-aminolactam **3**.

We had established[5] by n.m.r. spectroscopy that **3, 6,** and **7** are *N*-aminolactams and not azlactones (see also, Table III). Another proof is afforded by the Hearn–Chung reductive (catalytic hydrogenation) removal[16] of the *p*-nitrophenylamino group of **6** to give **38**, whose structure was established by the $J_{NH,2}$ coupling. The n.m.r. data of compound **36** and **37** (see Table III) prove their 3-azapyranosidic structure.

Whereas the ring expansion of all furanosic azoalcohols so far studied, proceeded regiospecifically, leading to the *N*-arylaminolactam having its nitrogen atom closer to the anomeric carbon atom, the same reaction applied to **C** gave, in poor yield, a mixture of both possible azaseptanosides (**39** and **40**).

These results show that furanos-3-uloses and furanosid-3-uloses* *p*-nitrophenylhydrazones can be regiospecifically converted into azapyranoses or pyranosides. This ring-expansion reaction, which maintains the stereochemistry at every asymmetric center and regiospecifically breaks the carbon chain, may provide a novel route to small chirons or biologically active chiral morpholines[17].

EXPERIMENTAL

General methods. — See ref. 18. U.v. spectra were recorded with a Uvicon 810 spectrophotometer, and c.d. curves, a JASCO J-20 spectropolarimeter; optical rotations were measured on solutions in chloroform with a Schmidt-Haentch polarimeter.

Methyl 3,5-O-isopropylidene-3-O-methyl-β-D-xylofuranoside (**8**). — A solution of methyl 3,5-*O*-isopropylidene-β-D-xylofuranoside[7] (5.1 g, 25 mmol) in *N,N*-dimethylformamide (50 mL) was added at 0°, under nitrogen, to sodium hydride (1.2 g, 50 mmol). After 30 min, CH_3I (5.5 mL, 88 mmol) was added. After 20 h at

*The same observation applies to furanosid-2-uloses (see ref. 15).

room temperature, the excess of sodium hydride was decomposed (MeOH), and the mixture was filtered through Celite. The filtrate was diluted with water (100 mL), the mixture extracted with $CHCl_3$ (4 × 50 mL), and the extracts were combined, and washed successively with 10% aqueous sodium thiosulfate solution (100 mL) and water (2 × 100 mL), dried ($MgSO_4$), and evaporated under vacuum. The residue was distilled at 61–71°/266 mPa to yield **1** (5 g, 92%) as a colorless syrup: $[\alpha]_D^{24}$ −33.5° (*c* 1.0); R_F 0.6 (9:1 $CHCl_3$–acetone); ν_{max}^{film} 1390 and 1380 (CMe_2) cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 1.40, 1.42 (2 s, 2 × 3 H, CMe_2), 3.42, 3.43 (2 s, 2 × 3 H, 2 CH_3O), 3.72 (~s, 1 H, $J_{1,2}$ <0.5, $J_{2,3}$ <0.2 Hz, H-2), 3.83 (dd, 1 H, $J_{5a,5b}$ 12.2, $J_{4,5a}$ 4.9 Hz, H-5a), 3.97 (dd, 1 H, $J_{4,5b}$ 4.9 Hz, H-5b), 4.15 (q, 1 H, $J_{3,4}$ 4.4 Hz, H-4), 4.22 (d, 1 H, H-3), and 4.92 (~s, 1 H, H-1); *m/z* 203 (15, $M^+ - Me^·$), 130 (10), 101 (20), 100 (100), 89 (23), 88 (63), 73 (28), 72 (68), 71 (47), and 70 (42).

Anal. Calc. for $C_{10}H_{18}O_5$ (218.25): C, 55.03; H, 8.31. Found: C, 54.89; H, 8.45.

Methyl 3,5-O-isopropylidene-3-O-methyl-α-D-xylofuranoside (**9**). — Compound **9** was prepared from methyl 3,5-*O*-isopropylidene-α-D-xylofuranoside[7] (2.37 g, 11.62 mmol), analogously to **8**. After distillation, **9** (1.65 g, 65%) was obtained as a syrup: b.p. 55°/266 mPa; $[\alpha]_D^{23}$ +105.3° (*c* 1.7); R_F 0.25 (1:1 Et_2O–hexane); ν_{max}^{film} 1390 and 1380 (CMe_2) cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 1.40, 1.43 (2 s, 2 × 3 H, CMe_2), 3.50 (s, 6 H, 2 MeO), 3.79 (dd, 1 H, $J_{4,5a}$ 5, $J_{5a,5b}$ 12 Hz, H-5a), 3.81 (dd, 1 H, $J_{1,2}$ 4.5, $J_{2,3}$ 2.5 Hz, H-2), 4.98 (dd, 1 H, $J_{4,5b}$ 4.8 Hz, H-5b), 4.15 (q, 1 H, $J_{3,4}$ 4.2 Hz, H-4), 4.30 (dd, 1 H, H-3), and 5.10 (d, 1 H, H-1); *m/z* 218 (0.24, M^+), 203 (19, $M^+ - Me^·$), 187 (5), 129 (7), 117 (5), 111 (11), 100 (100), 99 (5), 88 (65), 89 (25), 73 (32), 71 (52), and 59 (24).

Anal. Calc. for $C_{10}H_{18}O_5$ (218.25): C, 55.03; H, 8.31. Found: C, 54.98; H, 8.52.

Methyl 3-O-benzyl-3,5-O-isopropylidene-β-D-xylofuranoside (**10**). — To a solution of methyl 3,5-*O*-isopropylidene-β-D-xylofuranoside[7] (4.66 g, 22.8 mmol) in 1,4-dioxane (15 mL) was added powdered KOH (56 g, 400 mmol). The mixture was slowly warmed to its boiling point while benzyl chloride (22 mL, 191 mmol) was added dropwise. heating and vigorous stirring were continued for 4 h. The mixture was cooled to 70°, steam distilled, and then extracted with $CHCl_3$ (2 × 25 mL). The extracts were combined, successively washed with M H_2SO_4 (20 mL) and H_2O (20 mL), dried and evaporated, and the residue was purified by chromatography on a column of dry silica gel (1:4 AcOEt–hexane), to yield **10** (3.55 g, 94%) as a syrup: $[\alpha]_D^{20}$ −45° (*c* 1.3); R_F 0.37 (1:4 AcOEt–hexane); ν_{max}^{film} 1542, 1500 (Ph), 1380 and 1370 (CMe_2) cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 1.41 (s, 6 H, CMe_2), 3.44 (s, 3 H, OMe), 3.84 (dd, 1 H, $J_{5a,5b}$ 13, $J_{4,5a}$ 5 Hz, H-5a), 3.97 (d, 1 H, $J_{1,2}$ <1 Hz, H-2), 3.98 (dd, 1 H, $J_{4,5b}$ 5 Hz, H-5b), 4.17 (q, 1 H, $J_{3,4}$ 4.8 Hz, H-4), 4.24 (d, 1 H, H-3), 4.61 (s, 2 H, CH_2Ph), 4.99 (d, 1 H, H-1), and 7.34 (~s, 5 H, Ph); *m/z* 294 (17, M^+), 279 (10), 221 (4), 220 (26), 206 (11), 205 (77), 203 (7), 177 (4), 176 (4), 143 (8), 135 (8), and 91 (100).

Anal. Calc. for $C_{16}H_{22}O_5$ (294.35): C, 65.28; H, 7.53. Found: C, 64.99; H, 7.80.

Methyl 3-O-benzyl-3,5-O-isopropylidene-α-D-xylofuranoside (**11**). — Compound **11** was prepared from methyl 3,5-*O*-isopropylidene-α-D-xylofuranoside[4] (2.62 g, 12.8 mmol) analogously to **10**. Purification by chromatography on a column of dry silica gel afforded **11** (2.84 g, 74.7%) as a syrup, $[\alpha]_D^{20}$ +68.6° (*c* 0.98); R_F 0.5 (1:4 AcOEt–hexane); ν_{max}^{film} 1480, 1450 (Ph), 1380, and 1370 (CMe_2) cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 1.37 (s, 6 H, CMe_2), 3.50 (s, 3 H, OMe), 3.79 (dd, 1 H, $J_{5a,5b}$ 12.5, $J_{4,5a}$ 5 Hz, H-5a), 3.97 (dd, 1 H, $J_{4,5b}$ 4.5 Hz, H-5b), 4.00 (dd, 1 H, $J_{1,2}$ 4.2, $J_{2,3}$ 2 Hz, H-2), 4.18 (q, 1 H, $J_{3,4}$ 4.5 Hz, H-4), 4.30 (dd, 1 H, H-3), 4.64 (s, 2 H, OCH_2Ph), 5.03 (d, 1 H, H-1), and 7.25–7.45 (m, 5 H, Ph); *m/z* 294 (1.4, M^+), 215 (4), 205 (12), 156 (8), 143 (6), 135 (5), 129 (5), 115 (4), 91 (100), 85 (22), 75 (23), 59 (15), and 43 (31).

Anal. Calc. for $C_{16}H_{22}O_5$ (294.35): C, 65.28; H, 7.53. Found: C, 65.38; H, 7.35.

Methyl 2-O-benzyl-α-D-xylofuranoside (**12**). — A solution of **11** (4.7 g, 1.59 mmol) in 30% AcOH was heated for 4 h at 50°. Evaporation afforded **12** (4 g, 98%), which crystallized and was recrystallized from ether–hexane: m.p. 63–63.5°, $[\alpha]_D^{22}$ +129.84° (*c* 0.43); R_F 0.25 (Et_2O); ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 2.26 (bt, 1 H, $J_{5,OH}$ 7 Hz, O*H*-5), 2.92 (bd, 1 H, $J_{3,OH}$ 7 Hz, O*H*-3), 3.40 (s, 3 H, OMe), 3.87 (2 dd, 3 H, $J_{1,2}$ 4, $J_{2,3}$ 6, $J_{4,5}$ 4 Hz, H-2 and 2 H-5), 4.21 (dt, 1 H, $J_{3,4}$ 7 Hz, H-4), 4.57 (q, 1 H, H-3), 4.70 (AB, 2 H, J_{AB} 11.5 Hz, CH_2Ph), 4.80 (d, 1 H, H-1), and 7.30–7.45 (m, 5 H, Ph); *m/z* 223 (0.3), 163 (8), 135 (3), 103 (5), 93 (5), 92 (38), 91 (100), 79 (5), 77 (3), 73 (7), 65 (6), 61 (5), 57 (7), and 45 (3).

Anal. Calc. for $C_{13}H_{18}O_5$ (254.29): C, 61.41; H, 7.14. Found: C, 61.56; H, 7.36.

Methyl 5-O-benzoyl-2-O-methyl-β-D-xylofuranoside (**13**). — A solution of **8** (510 mg, 2.34 mmol) in 30% AcOH (20 mL) was heated for 1.5 h at 50°. After evaporation of the solvent, the dried residue was dissolved in pyridine (20 mL), and benzoyl chloride (0.35 mL, 3 mmol) was added at 0°. After 20 h at 0°, the mixture was treated with crushed ice (150 g), and extracted with $CHCl_3$ (4 × 50 mL). The extracts were combined, washed successively with M HCl (50 mL), saturated sodium hydrogencarbonate solution (2 × 50 mL), and H_2O (2 × 50 mL), dried, and evaporated, to give **13** (560 mg, 84%) as a syrup. An analytical sample was obtained by preparative, thick-layer chromatography; $[\alpha]_D^{24}$ −33.6° (*c* 1.0); R_F 0.52 (9:1 $CHCl_3$–acetone); ν_{max}^{film} 3500 (OH), 1720 (C=O), 1610, 1590, and 1455 (Ph) cm^{-1}; ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 2.95 (d, 1 H, $J_{3,OH}$ 12 Hz, OH), 3.43, 3.50 (2 s, 2 × 3 H, 2 MeO), 3.79 (d, 1 H, $J_{1,2}$ 0, $J_{2,3}$ 1 Hz, H-2), 4.25 (m, 1 H, H-3), 4.40–4.80 (m, 3 H, 2 H-5, H-4), 4.94 (s, 1 H, H-1), 7.38–7.59, and 8.00–8.16 (2 m, 3 H, 2 H, Ph,); *m/z* 251 (3), 205 (14), 105 (100), 101 (65), 100 (79), 88 (30), 87 (67), 77 (49), 75 (25), and 71 (58).

Anal. Calc. for $C_{14}H_{18}O_6$ (289.3): C, 59.57; H, 6.43. Found: C, 59.43; H, 6.38.

Methyl 5-O-benzoyl-3-O-methyl-α-D-xylofuranoside (**14**). — This was obtained from **9**, analogously to **13**; yield 56%, syrup: $[\alpha]_D^{28}$ +119.3° (*c* 1.25); R_F 0.35

(9:1 $CHCl_3$–acetone); ν_{max}^{film} 3480 (OH), 1725 (C=O), 1640, and 1610 (Ph) cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 3.10 (d, 1 H, $J_{3,OH}$ 5 Hz, OH), 3.47, 3.50 (2 s, 2 × 3 H, OMe), 3.82 (t, 1 H, $J_{1,2'} = J_{2,3}$ 5.1 Hz, H-2), 4.35–4.52 (m, 3 H, 2 H-5, H-3), 4.66–4.80 (m, 1 H, H-4), 5.02 (d, 1 H, H-1), 7.37–7.63, and 8.00–8.10 (2 m, 3 H, 2 H, Ph); *m/z* 281 (1.6), 251 (25), 177 (4), 123 (8), 100 (100), 87 (90), 77 (75), 71 (93), 57 (32), and 51 (52).

Anal. Calc. for $C_{14}H_{18}O_6$ (289.3): C, 59.57; H, 6.43. Found: C, 59.31; H, 6.36.

*Methyl 2-O-benzyl-3,5-O-benzylidene-β-*D*-xylofuranoside* (**15**). — To a solution of methyl 2-*O*-benzyl-β-D-xylofuranoside (1.5 g, 5.9 mmol; obtained by acid hydrolysis of **10**) in anhydrous *N,N*-dimethylformamide (4.5 mL) were added *p*-toluenesulfonic acid hydrate (3.5 mg) and α,α-dimethoxytoluene (943 mg, 6.2 mmol). After 40 min of reflux at 60° under vacuum, the *N,N*-dimethylformamide was distilled off at 90° under vacuum. The mixture was cooled, and, after addition of 0.05M sodium hydrogencarbonate (10 mL), extracted with $CHCl_3$ (2 × 50 mL). The extracts were combined, washed with H_2O (20 mL), dried ($MgSO_4$), and evaporated, to give **15** (1.5 g, 75%) having the physical properties described by Lipták *et al.*[10].

*Methyl 2-O-benzyl-3,5-O-benzylidene-α-*D*-xylofuranoside* (**16**). — This was prepared similarly to **15** from **12**; yield 75%. Its physical properties were as described by Lipták *et al.*[10].

*Methyl 2,5-di-O-benzyl-β-*D*-xylofuranoside* (**17**). — Compound **17** was prepared as described by Lipták *et al.*[10]; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 2.92 (bs, 1 H, OH), 3.37 (s, 3 H, OMe), 3.63 (q, 1 H, $J_{5a,5b}$ 10, $J_{4,5a}$ 3.5 Hz, H-5a), 3.77 (q, 1 H, $J_{4,5b}$ 3.5 Hz, H-5b), 3.87 (d, 1 H, $J_{2,3}$ 1 Hz, H-2), 4.17 (q after irradiation of OH, 1 H, $J_{3,4}$ 2.8 Hz, H-3), 4.44 (q, 1 H, H-4), 4.55 (s, 4 H, 2 CH_2Ph), 4.9 (s, 1 H, H-1), and 7.17–7.35 (m, 10 H, Ph); the other physical properties were as described[10].

*Methyl 5-O-benzoyl-3-O-methyl-β-*D*-*erythro*-pentofuranosid-3-ulose* (**19**). — To a mixture of CH_2Cl_2 (500 mL) and dry pyridine (33.5 mL) was added CrO_3 (21.22 g) at 25° under nitrogen. After 30 min at 25°, **13** (5.01 g, 17.7 mmol) was added. After 40 min, saturated sodium hydrogencarbonate solution (80 mL) was added, and the organic layer was washed with H_2O (3 × 50 mL), dried ($MgSO_4$), and evaporated. Crystallization (ether) of the residue afforded **19** (1.98 g, 40%); m.p. 102.3–103.5°, $[\alpha]_D^{25}$ −94.47° (*c* 1.08); R_F 0.59 (Et_2O); ν_{max}^{KBr} 1775 (C=O), 1725 (CO–Ph), 1610, 1475, 1460, and 1442 (Ph) cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 3.50, 3.67 (2 s, 2 × 3 H, 2 MeO), 4.27 (d, 1 H, $J_{1,2}$ 5 Hz, H-2), 4.52 (dd, 1 H, $J_{4,5a}$ 8, $J_{4,5b}$ 3.5 Hz, H-4), 4.56 (dd, 1 H, $J_{5a,5b}$ −13 Hz, H-5a), 4.68 (dd, 1 H, H-5b), 5.30 (d, 1 H, H-1), 7.4–7.66, and 8.05–8.15 (2 m, 3 H, 2 H, Ph); *m/z* 249 (0.7), 220 (11), 205 (4), 158 (2), 137 (4), 126 (11), 122 (11), 105 (100), 88 (16), 77 (33), 73 (11), and 51 (14).

Anal. Calc. for $C_{14}H_{16}O_6$ (280.28): C, 60.0; H, 5.75. Found: C, 60.08; H, 5.85.

*Methyl 5-O-benzoyl-3-O-methyl-α-*D*-*erythro*-pentofuranosid-3-ulose* (**20**). —

Compound **20** was prepared from **14** (1.45 g, 5.14 mmol) as described for the preparation of **19**. After crystallization and recrystallization (ether), **20** (580 mg, 40%) was obtained: m.p. 105.9–106.9°, $[\alpha]_D^{20}$ +268.6° (*c* 1.07); ν_{max}^{KBr} 1780 (C=O), 1720 (COPh), 1610, 1590, and 1455 (Ph) cm^{-1}; ^1H-n.m.r. (90 MHz, $CDCl_3$): δ 3.53, 3.62 (2 s, 2 × 3 H, 2 MeO), 4.07 (bd, 1 H, $J_{1,2}$ 4.7, $J_{2,4}$ 0.9 Hz, H-2), 4.28 (td, 1 H, $J_{4,5a}$ 3.3, $J_{4,5b}$ 2.9 Hz, H-4), 4.48 (dd, 1 H, $J_{5a,5b}$ 12 Hz, H-5a), 4.77 (dd, 1 H, H-5b), 5.30 (d, 1 H, H-1), 7.33–7.60, and 7.90–8.02 (2 m, 3 H, 2 H, Ph); *m/z* 220 (5), 205 (1), 158 (1), 137 (2), 122 (11), 105 (100), 98 (2), 88 (20), 77 (29), 73 (14), 55 (5), and 51 (12).

Anal. Calc. for $C_{14}H_{16}O_6$ (280.28): C, 60.0; H, 5.75. Found: C, 60.16; H, 5.90.

*Methyl 5-O-benzoyl-3-O-methyl-α-*D-erythro*-pentofuranosid-3-ulose* p-*nitrophenylhydrazone* (**21**). — A solution of **20** (510 mg, 1.82 mmol) and *p*-nitrophenylhydrazine (278 mg, 1.82 mmol) in methanol (35 mL) was refluxed for 1 h, and then evaporated. Crystallization and recrystallization from ethanol afforded **21** (*E* + *Z*): m.p. 98–103°; R_F 0.48 (Et_2O); ν_{max}^{KBr} 3280 (NH), 1772 (C=O), 1595, and 1330 (NO_2) cm^{-1}; ^1H-n.m.r. ($CDCl_3$, 200 MHz): *E* isomer: δ 3.46, 3.72 (2 s, 2 × 3 H, 2 MeO), 4.22 (dd, 1 H, $J_{4,5a}$ 6.5, $J_{5a,5b}$ 12.5 Hz, H-5a), 4.45 (dd, 1 H, $J_{1,2}$ 5.0, $J_{2,4}$ 2.0 Hz, H-2), 4.87–5.01 (m, 2 H, H-4,5b), 5.15 (d, 1 H, H-1), 7.18–7.20, 8.12–8.22 (2 m, 2 × 2 H, *p*-PhNO_2), 7.48–7.56, 7.65–7.72 (2 m, 2 H, 3 H, Ph), and 9.62 (s, 1 H, NH); *Z* isomer: δ 3.59, 3.60 (2 s, 2 × 3 H, 2 MeO), 4.53 (dd, 1 H, $J_{4,5a}$ 5, $J_{5a,5b}$ 7 Hz, H-5a), 4.69 (dd, 1 H, $J_{1,2}$ 4, $J_{2,4}$ 2 Hz, H-2), 4.80 (dd, 1 H, $J_{4,5b}$ 2.5 Hz, H-5b), 4.84 (ddd, 1 H, H-4), 5.29 (d, 1 H, H-1), 6.90–7.02, 8.05–8.15 (2 m, 2 × 2 H, *p*-PhNO_2), 7.40–7.60, 8.00–8.20 (2 m, 2 H, 3 H, Ph), and 9.63 (bs, 1 H, NH); *m/z* 415 (34, M^+), 293 (33), 261 (33), 233 (34), 220 (12), 218 (17), 205 (26), 194 (14), 193 (100), and 105 (24).

Anal. Calc. for $C_{20}H_{21}N_3O_7$ (415.41): C, 57.83; H, 5.10; N, 10.12. Found: C, 57.87; H, 5.20; N, 10.25.

*Methyl 2,5-di-O-benzyl-β-*D-erythro*-pentofuranosid-3-ulose* (**22**). — To a solution of **17** (1.5 g, 4.3 mmol) in CCl_4 (40 mL) were added, saturated aqueous sodium hydrogencarbonate (40 mL) and ruthenium dioxide hydrate (60 mg). The mixture was stirred vigorously, and then 5% sodium periodate was added dropwise until no more starting material could be detected by t.l.c. After addition of a few drops of 2-propanol, the mixture was filtered, the organic layer was separated, and the aqueous layer was evaporated. The residue was extracted with CH_2Cl_2 (3 × 20 mL), and the extracts were combined and evaporated to afford **22** (1.3 g, 88%) as a syrup which was characterized by i.r. and ^1H-n.m.r. spectroscopy and by the preparation of its 4-nitrophenylhydrazone (**24**): R_F 0.70 (3:1 Et_2O–hexane); ν_{max}^{film} 1770 (C=O) cm^{-1}; ^1H-n.m.r. (200 MHz, $CDCl_3$): δ 3.50 (s, 3 H, OMe), 3.68 (dd, 1 H, $J_{5a,5b}$ 11, $J_{4,5a}$ 5 Hz, H-5a), 3.75 (dd, 1 H, $J_{4,5b}$ 3 Hz, H-5b), 3.90 (dd, 1 H, $J_{1,2}$ 4, $J_{2,4}$ 1 Hz, H-2), 4.35 (qd, 1 H, H-4), 4.60 (AB, 2 H, CH_2Ph), 4.82 (AB, 2 H, CH_2Ph), 5.07 (d, 1 H, H-1), and 7.30–7.45 (m, 10 H, Ph).

*Methyl 2,5-di-O-benzyl-α-*D-erythro*-pentofuranosid-3-ulose* (**23**). — Compound **23** was prepared from **18** (530 mg, 1.54 mmol) by the method described for

22. Crystalline **23** (500 mg, 86%) was obtained, and recrystallized from ether–hexane: m.p. 40.5–41.5°, $[\alpha]_D^{22}$ +143.6° (*c* 1.07); ν_{max}^{KBr} 1770 (C=O) cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 3.40 (s, 3 H, OMe), 3.68 (d, 2 H, $J_{4,5}$ 2.1 Hz, 2 H-5), 4.05 (bt, 1 H, H-4), 4.20 (dd, 1 H, $J_{1,2}$ 4.3, $J_{2,4}$ 0.8 Hz, H-2), 4.47 (AB, 2 H, CH_2Ph), 4.77 (AB, 2 H, CH_2Ph), 5.01 (d, 1 H, H-1), and 7.15–7.30 (m, 10 H, 2 Ph); *m/z* 282 (0.4), 253 (0.8), 191 (20), 181 (35), 161 (30), 145 (10), 135 (25), 107 (60), and 91 (100).

Anal. Calc. for $C_{20}H_{22}O_5$ (342.40): C, 70.16; H, 6.48. Found: C, 70.30; H, 6.64.

*Methyl 2,5-di-*O*-benzyl-β-*D-erythro*-pentofuranosid-3-ulose* p-*nitrophenylhydrazone* (**24**). — Compound **24** was prepared from **22** (1.3 g, 3.8 mmol) and *p*-nitrophenylhydrazine (0.58 g, 3.8 mmol) in methanol (50 mL) by the procedure described for **21**. After crystallization and recrystallization (methanol), **24** (1.1 g, 61%) was obtained: m.p. 115–126°; R_F 0.55 and 0.62 (3:2 Et_2O–hexane); ν_{max}^{KBr} 3240 (NH), 1590, and 1329 (NO_2) cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): *E* isomer: δ 3.37 (s, 3 H, OMe), 3.82 (t, 1 H, $J_{5a,5b}$, $J_{4,5a}$ 9 Hz, H-5a), 3.94 (dd, 1 H, $J_{4,5b}$ 4.5 Hz, H-5b), 4.27 (s, 1 H, H-2), 4.62 (AB, 2 H, CH_2Ph), 4.78 (AB, 2 H, CH_2Ph), 4.92 (m, 1 H, H-4), 5.00 (s, 1 H, H-1), 6.25–6.53, 7.87–8.05 (2 m, 2 × 2 H, *p*-$PhNO_2$), 7.11–7.57 (m, 10 H, 2 Ph), and 9.97 (s, 1 H, NH); *Z* isomer: δ 3.50 (s, 3 H, OMe), 3.66 (q, 1 H, $J_{5a,5b}$ 10.2, $J_{4,5a}$ 7 Hz, H-5a), 3.80 (q, 1 H, $J_{4,5b}$ 3.5 Hz, H-5b), 4.55 (dd, 1 H, $J_{1,2}$ 3, $J_{2,4}$ 2.1 Hz, H-2), 4.56–4.78 (m, 2 × 2 H, 2 CH_2Ph), 4.84 (ddd, 1 H, H-4), 5.17 (d, 1 H, H-1), 6.68–6.77, 8.06–8.25 (2 m, 2 × 2 H, *p*-$PhNO_2$), 7.11–7.57 (m, 10 H, 2 Ph), and 8.44 (s, 1 H, NH); *m/z* 477 (22, M^+), 357 (21), 326 (25), 281 (20), 248 (25), 218 (50), 164 (20), 122 (28), 108 (31), and 91 (100).

Anal. Calc. for $C_{26}H_{27}N_3O_6$ (477.52): C, 65.40; H, 5.70; N, 8.80. Found: C, 65.49; H, 5.50; N, 8.77.

*Methyl 2,5-di-*O*-benzyl-α-*D-erythro*-pentofuranosid-3-ulose* p-*nitrophenylhydrazone* (**25**). — Compound **25** was prepared from **23** (480 mg, 1.40 mmol) by the procedure described for **21**. After crystallization and recrystallization (ethanol), **25** (450 mg, 67%) was obtained: m.p. 98–100°; R_F 0.63 and 0.68 (ether); ν_{max}^{KBr} 3250 (NH), 1599, and 1350 (NO_2) cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): *E* isomer: δ 3.42 (s, 3 H, OMe), 3.63 (dd, 1 H, $J_{5a,5b}$ 8.5, $J_{4,5a}$ 8.4 Hz, H-5a), 3.79 (dd, 1 H, $J_{4,5b}$ 3.2 Hz, H-5b), 4.52 (dd, 1 H, $J_{1,2}$ 4.5, $J_{2,4}$ 2 Hz, H-2), 4.60 (AB, 2 H, CH_2Ph), 4.75 (dt, 1 H, H-4), 4.85 (d, 1 H, H-1), 4.95 (AB, 2 H, CH_2Ph), 6.40–6.50 and 7.88–8.00 (2 m, 2 × 2 H, *p*-$PhNO_2$), 7.26–7.50 (m, 10 H, 2 Ph), and 9.70 (s, 1 H, NH); *Z* isomer: δ 3.47 (s, 3 H, OMe), 3.69 (dd, 1 H, $J_{5a,5b}$ 11.5, $J_{4,5a}$ 5.2 Hz, H-5a), 3.81 (dd, 1 H, $J_{4,5b}$ 2.5 Hz, H-5b), 4.53 (AB, 2 H, CH_2Ph), 4.63 (dd, 1 H, $J_{2,4}$ 4.5 Hz, H-4), 4.70 (AB, 2 H, CH_2Ph), 4.80 (dd, 1 H, $J_{1,2}$ 4.5 Hz, H-2), 5.26 (d, 1 H, H-1), 6.70–6.78 and 8.02–8.10 (2 m, 2 × 2 H, *p*-$PhNO_2$), 7.25–7.50 (m, 10 H, 2 Ph), and 9.60 (s, 1 H, NH); *m/z* 477 (1, M^+), 371 (0.5), 339 (1.6), 326 (5), 296 (0.8), 280 (5.8), 262 (0.8), 248 (5), 218 (42), 202 (4.4), 190 (7.2), 164 (5.5), 150 (7.2), 105 (1.6), and 91 (100).

Anal. Calc. for $C_{26}H_{27}N_3O_6$ (477.52): C, 65.40; H, 5.70; N, 8.80. Found: C, 65.58; H, 5.53; N, 8.75.

Methyl 3-O-acetyl-5-O-benzoyl-3-C-(p-nitrophenylazo)-α-D-xylo- and -ribo-furanoside (**26** *and* **27**). — To lead tetraacetate (2 mmol) (dried for 1 h over KOH under vacuum) in CH_2Cl_2 (25 mL) was slowly added a solution of **21** (830 mg, 2 mmol) in CH_2Cl_2 (30 mL) at 0° under nitrogen. After 20 h at room temperature, 3 drops of ethylene glycol were added, followed by ice–water (50 mL). The organic layer was decanted, washed with H_2O (2 × 25 mL), dried ($MgSO_4$), and evaporated, to give a syrup which was a mixture of **26** and **27**. Thick-layer preparative chromatography (Et_2O) gave **26** (470 mg) and **27** (100 mg) (yield: 60%). Compound **26**: m.p. 144–145.3°, $[\alpha]_D^{24.5}$ +131° (*c* 0.36); R_F 0.67 (Et_2O); λ_{max}^{EtOH} 230 (ε 12800), 282 nm (15200); ν_{max}^{KBr} 1745, 1715 (C=O), 1525, 1345 (NO_2), and 1450 (N=N) cm^{-1}; for ^1H-n.m.r. and ^{13}C-n.m.r. data, see Table I; *m/z* 442 (0.2), 323 (28), 263 (22), 249 (25), 235 (35), 193 (29), 165 (21), 127 (68), 105 (100), 77 (18), and 88 (10).

Anal. Calc. for $C_{22}H_{23}N_3O_9$ (473.44): C, 55.81; H, 4.90; N, 8.88. Found: C, 55.96; H, 5.15; N, 8.93.

Compound **27**: syrup; $[\alpha]_D^{21.5}$ +13° (*c*, 0.4); R_F 0.78 (Et_2O); λ_{max}^{EtOH} 230 (ε 11637), 282 nm (13681); ν_{max}^{film} 1720 (C=O), 1570, 1525, 1350 ($\nu_{as}NO_2$, ν_sNO_2), and 1450 (N=N) cm^{-1}; for ^1H- and ^{13}C-n.m.r., see Table I; *m/z* 442 (0.15, M^+ − OMe), 323 (1), 293 (1), 263 (1), 249 (9), 235 (11), 193 (10), 127 (70), 105 (100), 88 (8), and 77 (18).

Anal. Calc. for $C_{22}H_{23}N_3O_9$ (473.44): C, 55.81; H, 4.90; N, 8.88. Found: C, 55.98; H, 4.99; N, 9.01.

Methyl 3-O-acetyl-2,5-di-O-benzyl-3-C-(p-nitrophenylazo)-β-D-xylo- and -ribo-furanosides (**28** *and* **29**). — Compounds **28** and **29** were prepared from **24** (478 mg, 1 mmol) by the procedure described for **26** and **27**. A 3:1 mixture (430 mg, 80%) of **28** and **29** was obtained, and purified by thick-layer, preparative chromatography (1:1 Et_2O–hexane).

Compound **28**: syrup; $[\alpha]_D^{24}$ +40.3° (*c* 0.79); R_F 0.52 (2:1 Et_2O–hexane); λ_{max}^{EtOH} 205 (ε 26600) and 285 nm (15500); ν_{max}^{film} 1755 (C=O), 1530, 1350 ($\nu_{as}NO_2$, ν_sNO_2), and 1450 (N=N) cm^{-1}; for ^1H- and ^{13}C-n.m.r.; see Table I; *m/z* 293 (1), 263 (3), 221 (2), 203 (25), 193 (4), 187 (13), 181 (94), 173 (6), 150 (4.5), 122 (17), 105 (12), 103 (4.5), and 91 (100).

Anal. Calc. for $C_{28}H_{29}N_3O_8$ (535.56): C, 62.80; H, 5.46; N, 7.85. Found: C, 62.74; H, 5.47; N, 7.77.

Compound **29**: syrup; $[\alpha]_D^{23}$ −55.26° (*c* 0.40); R_F 0.58 (2:1 Et_2O–hexane); λ_{max}^{EtOH} 205 (ε 27500) and 283 nm (13700); ν_{max}^{film} 1750 (C=O), 1522, 1342 ($\nu_{as}NO_2$, ν_sNO_2), and 1450 (N=N) cm^{-1}; for ^1H- and ^{13}C-n.m.r., see Table I; *m/z* 293 (1), 263 (1), 221 (1), 203 (14), 193 (2), 187 (8), 181 (50), 173 (3), 150 (3), 127 (6), 122 (9), 103 (6), and 91 (100).

Anal. Calc. for $C_{28}H_{29}N_3O_8$ (535.56): C, 62.80; H, 5.46; N, 7.85. Found: C, 63.03; H, 5.75; N, 7.59.

Methyl 3-O-acetyl-2,5-di-O-benzyl-3-C-(p-nitrophenylazo)-α-D-xylo- and -ribo-furanosides (**30** *and* **31**). — Compounds **30** and **31** were prepared from **25** (420 mg, 0.88 mmol) by the procedure described for **26** and **27**. The 1:2 mixture of

30 and **31** (430 mg, 91%) was separated by preparative, thick-layer chromatography (2:1 Et_2O–hexane).

Compound **30**: syrup; $[\alpha]_D^{26}$ +105.5° (*c* 2); R_F 0.30 (2:1 Et_2O–hexane); λ_{max}^{EtOH} 205 (ε 26200) and 284 nm (12800); ν_{max}^{film} 1750 (C=O), 1525, 1350 ($\nu_{as}NO_2$, ν_sNO_2), and 1450 (N=N) cm^{-1}; for ^1H- and ^{13}C-n.m.r., see Table I; *m/z* 324 (1), 311 (2), 219 (6), 203 (12), 181 (95), 122 (26), 105 (47), 91 (100), 77 (29), 65 (51), and 55 (16).

Compound **31**: syrup; $[\alpha]_D^{25}$ −62° (*c* 0.9); R_F 0.40 (2:1 Et_2O–hexane); λ_{max}^{EtOH} 205 (ε 20900) and 286 nm (9400); ν_{max}^{film} 1750 (C=O), 1525, 1349 ($\nu_{as}NO_2$, ν_sNO_2), and 1455 (N=N) cm^{-1}; for ^1H- and ^{13}C-n.m.r., see Table I; *m/z* 324 (1), 311 (3), 294 (1), 284 (1), 278(1), 263 (1), 181 (8), and 91 (100).

Anal. Calc. for $C_{28}H_{29}N_3O_8$ (535.56): C, 62.80; H, 5.46; N, 7.85. Found: C, 62.94; H, 5.52; N, 7.67.

General procedure for preparation of azoalcohols. — A solution of azoacetates in anhydrous MeOH was treated by sodium methoxide to alkalinity (pH paper). After 6 h at room temperature, the base was neutralized (Dowex 50, H^+), the suspension filtered, and the filtrate evaporated. The residue was purified by chromatography on a column of dry silica gel. Azoacetates **28** to **31** afforded unstable syrups (**32** to **35**), characterized by ^1H-n.m.r. spectroscopy (see Table I).

*3-Aza-3-deoxy-1,2-O-isopropylidene-3-(*p*-nitrophenylamino)-α-*L*-glycero-pentopyranos-4-ulose* (**3**). — To a solution of **2** (ref. 6; 140 mg, 0.45 mmol) in anhydrous THF (15 mL) was added *tert*-BuOK to alkalinity. After 20 h at 20°, the solution was washed with aqueous saturated solution of NH_4Cl (20 mL), dried ($MgSO_4$), and evaporated, and the residue was purified by thick-layer chromatography (solvent: Et_2O) to afford **3** (45 mg, 32%): m.p. 132–134°, $[\alpha]_D^{24}$ −94.4° (*c* 0.8); R_F 0.52 (Et_2O); λ_{max}^{EtOH} 204 (ε 7800), 219 (6640), and 336 nm (13800); ν_{max}^{KBr} 3305 (NH), 1710 (C=O), 1502 and 1335 (ν_{as}, ν_sNO_2) cm^{-1}; for ^1H- and ^{13}C-n.m.r., see Table III; *m/z* 309 (15, M^+), 294 (8, $M^+ - Me^\cdot$), 251 (100), 235 (17), 222 (40), 176 (25), 165 (21), 150 (21), 137 (14), and 122 (25).

Anal. Calc. for $C_{13}H_{15}N_3O_6$ (309.28): C, 50.49; H, 4.89; N, 13.60. Found: C, 50.47; H, 5.06; N, 13.50.

*Methyl 3-aza-2,6-di-O-benzyl-3-deoxy-3-(*p*-nitrophenylamino)-β-*D*-ribo-hexoyranosid-4-ulose* (**36**). — A solution of **32** and **33** (310 mg, 0.62 mmol) in anhydrous THF (30 mL) was treated as described for **3**. The residue was purified by preparative, thick-layer chromatography to give **36** (90 mg, 29%) as a syrup: $[\alpha]_D^{24}$ −62.7° (*c* 0.59); R_F 0.34 (4:1 Et_2O–hexane); λ_{max}^{EtOH} 206 (ε 22200) and 342 nm (10500); ν_{max}^{film} 3280 (NH), 1685 (C=O), 1500, and 1330 (ν_{as}, ν_sNO_2) cm^{-1}; for ^1H- and ^{13}C-n.m.r., see Table III; *m/z* 493 (4.5, M^+), 295 (4.5), 242 (8.4), 226 (26.5), 207 (9.5), 181 (18.2), 164 (6.7), 150 (16.2), 138 (23.5), 122 (17.9), 105 (11.7), and 91 (100).

Anal. Calc. for $C_{26}H_{27}N_3O_7$ (493.52): C, 63.28; H, 5.51; N, 8.51. Found: C, 63.11; H, 5.72; N, 8.40.

*Methyl 3-aza-2,6-di-O-benzyl-3-deoxy-3-(*p*-nitrophenylamino)-α-*D*-ribo-

hexopyranosid-4-ulose (**37**). — Upon attempted chromatographic separation on a preparative, thick-layer chromatographic plate (Merck) with 2:1 Et_2O–hexane a mixture of **34** and **35** (128 mg, 0.26 mmol) was transformed into **37** (80 mg, 62%), isolated as an amorphous solid: $[\alpha]_D^{22}$ +27.2° (*c* 0.99); R_F 0.10 (2:1 Et_2O–hexane); λ_{max}^{EtOH} 205 (ε 24200) and 346 nm (11500); ν_{max}^{KBr} 3300 (NH), 1685 (C=O), 1500, and 1330 (ν_{as}, $\nu_s NO_2$) cm^{-1}; for ^1H- and ^{13}C-n.m.r., see Table III; *m/z* 493 (1.5, M^+), 242 (1.4), 226 (5.4), 207 (3.1), 181 (2.2), 164 (0.7), 150 (1.7), 138 (3.1), 107 (14), 99 (8.5), and 91 (100).

Anal. Calc. for $C_{26}H_{27}N_3O_7$ (493.52): C, 63.28; H, 5.51; N, 8.51. Found: C, 63.37; H, 5.56; N, 8.49.

*3-Aza-3-deoxy-1,2:6,7-di-*O*-isopropylidene-3-(*p*-nitrophenylamino)-α-*D*-ribo-hepto-1,5-pyranos-4-ulose* (**6**). — Compound **6** was prepared from **5** (500 mg, 1.1 mmol) by the procedure described for **3**. Purification by preparative thick-layer chromatography gave **6** (256 mg, 57%): m.p. 168.0–169.1°; $[\alpha]_D^{24}$ +52.8° (*c* 1.39); R_F 0.42 (1:1 hexane–ethyl acetate); λ_{max}^{EtOH} 218 (ε 8900) and 340 nm (12200); ν_{max}^{KBr} 3310 (NH), 1705 (C=O), 1502, and 1330 (ν_{as}, $\nu_s NO_2$) cm^{-1}; for ^1H- and ^{13}C-n.m.r., see Table III; *m/z* 409 (10, M^+), 394 (23, $M^+ - Me^\cdot$), 351 (53), 322 (4.6), 308 (2), 293 (21), 264 (16), 235 (53), 218 (100), 194 (40), 138 (29), 101 (47), 85 (53), 59 (40), and 43 (70).

Anal. Calc. for $C_{18}H_{23}N_3O_8$ (409.40): C, 52.81; H, 5.66; N, 10.26. Found: C, 52.72; H, 5.60; N, 10.21.

*3-Aza-3-deoxy-1,2:6,7-di-*O*-isopropylidene-3-(*N*-p-nitrophenylacetamido)-α-*D*-ribo-hepto-1,5-pyranos-4-ulose* (**7**). — To a solution of **6** (178 mg, 0.43 mmol) in triethylamine (8 mL) was added acetic anhydride (4 mL). After 2 h at 20°, the mixture was treated with crushed ice (10 g) and extracted with $CHCl_3$ (3 × 10 mL); the extracts were combined, dried ($MgSO_4$), and evaporated, and the residue was purified by preparative chromatography on silica gel (ether) to give **7** (160 mg, 82%) as an amorphous solid: $[\alpha]_D^{23.5}$ +63.9° (*c* 0.94); R_F 0.58 (Et_2O); λ_{max}^{EtOH} 205.2 (ε 10500) and 289 nm (9200); ν_{max}^{film} 1710 (C=O), 1522, and 1346 (ν_{as}, $\nu_s NO_2$) cm^{-1}; ^1H-n.m.r. (90 MHz, $CDCl_3$) at 35°: 2 series of signals, corresponding to a 5:3 ratio of isomer a:isomer b, see Table III; *m/z* 436 (85, $M^+ - Me^\cdot$), 393 (85), 351 (25), 335 (12), 293 (20), 277 (15), 235 (22), 218 (25), 97 (60), 83 (62), 81 (57), 69 (100), and 57 (97).

Anal. Calc. for $C_{20}H_{25}N_3O_9$ (451.44): C, 53.21; H, 5.58; N, 9.31. Found: C, 53.21; H, 5.66; N, 9.24.

*3-Aza-3-deoxy-1,2:6,7-di-*O*-isopropylidene-α-*D*-ribo-hepto-1,5-pyranos-4-ulose* (**38**). — A solution of **6** (200 mg, 0.48 mmol) in a mixture of ethanol (25 mL) and AcOH (2 mL) was treated overnight in a Paar hydrogenator under hydrogen at 304 kPa in the presence of 10% Pd–C catalyst (80 mg). After filtration and evaporation, the residue was purified by flash chromatography, to give **38** (110 mg, 82%): m.p. 155.0–156.2°, $[\alpha]_D^{22}$ +99° (*c* 1.04); R_F 0.4 (Et_2O); λ_{max}^{EtOH} 203 (ε 2500) and 270 nm (273); ν_{max}^{KBr} 3330 (NH) and 1688 (C=O) cm^{-1}; for ^1H- and ^{13}C-n.m.r., see Table III; *m/z* 258 (22, $M^+ - Me^\cdot$), 200 (20), 173 (12), 158 (12), 128 (12), 115 (26), 101 (28), 86 (38), 73 (23), 59 (100), and 55 (85).

Anal. Calc. for $C_{12}H_{19}NO_6$ (273.28): C, 52.74; H, 7.01; N, 5.13. Found: C, 52.88; H, 6.93; N, 5.08.

*Methyl 4-aza-7-deoxy-2,3-O-isopropylidene-4-(p-nitrophenylamino)-β-*L*-lyxo-hepto-1,6-septanosid-5-ulose* (**39**) *and methyl 5-aza-7-deoxy-2,3-O-isopropylidene-5-(p-nitrophenyl)-β-*L*-lyxo-hepto-1,6-septanosid-4-ulose* (**40**). — Treated as described for **3**, methyl 6-deoxy-2,3-*O*-isopropylidene-4-*C*-(*p*-nitrophenylazo)-β-L-manno-pyranoside[6] (250 mg, 0.68 mmol) gave, after preparative, thick-layer chromatography, 43.5 mg (17.4%) of a mixture of **39** and **40** in the ratio of 7:3; m.p. 102–115°; R_F 0.6 (5:1 diisopropyl ether–MeOH); ν_{max}^{KBr} 3310 (NH), 1705 (C=O), 1600, and 1335 (ν_{as}, $\nu_s NO_2$) cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): compound **39**: δ 1.47, 1.50 (2 s, 2 × 3 H, CMe_2), 1.55 (d, 3 H, $J_{6,Me}$ 6 Hz, Me), 3.58 (s, 3 H, OMe), 4.50 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 7 Hz, H-2), 4.55 (d, 1 H, H-3), 5.27 (d, 1 H, H-1), 5.55 (q, 1 H, H-6), 5.56 (s, 1 H, NH), 6.75–6.85, and 8.05–8.15 (2 m, 2 × 2 H, Ph); compound **40**: δ 1.55 (d, 3 H, $J_{6,Me}$ 6 Hz, Me), 1.60, 1.65 (2 s, 3 H, CMe_2), 3.58 (s, 3 H, OMe), 4.34 (q, 1 H, $J_{1,2}$ 6, $J_{2,3}$ 10 Hz, H-2), 4.75 (d, 1 H, H-3), 4.86 (d, 1 H, H-1), 5.55 (q, 1 H, H-6), 6.56 (s, 1 H, NH), 6.75–6.85, and 8.05–8.15 (2 m, 2 × 2 H, Ph).

Anal. Calc. for $C_{16}H_{21}N_3O_7$ (367.36): C, 52.31; H, 5.76; N, 11.44. Found: C, 52.40; H, 5.94; N, 11.57.

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