148. Synthesis and Enzymatic Evaluation of Substrates and Inhibitors of β-Glucuronidases

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The phosphono and the tetrazolyl analogues **4** and **5** of 4-methylumbelliferyl β-D-glucuronide (= (4-methyl-2-oxo-2*H*-1-benzopyran-7-yl β-D-glucopyranosid)uronic acid; **6**) were synthesized and evaluated as substrates of β-glucuronidases. Similarly, the phenylcarbamate **7** and its phosphono analogue **8** were prepared and evaluated as inhibitors. To examine the diastereoselectivity of the phosphorylation, we also synthesized the protected L-*ido*-, D-*gluco*-, and D-*galacto*-configurated phospha-glycopyranuronates **12**, **13**, **21**, **22**, **34** and **35**. Two strategies were followed. In the first one, the glucuronic acid **19** was decarboxylated to **11** and further transformed, *via* **20**, into the trichloroacetimidate **10** (*Scheme 2*). Phosphorylation of **10** with $(MeO)_3P$ yielded the diastereoisomers **12** and **13**, the diastereoselectivity depending on the solvent. In MeCN, **12** and **13** were obtained in a ratio of 1:1, while in non-participating solvents the L-*ido* **12** was by far the major diastereoisomer. The acetate **11** was inert to $(MeO)_3P$, but reacted with $(PhO)_3P$ to the anomeric mixture **21**/**22**, in keeping with a stabilizing 1,3-interaction in the intermediate phosphonium salt. Similarly, the phospha-galacturonates **34** and **35** were prepared from the galactoside **23** *via* the enol ether **26**, the lactone **27**, and the acetates **28**/**29** that were also transformed into the trichloroacetimidate **33** (*Scheme 3*). In the second, higher-yielding strategy, phosphorylation of the pentodialdehyde **39** to **40**/**41** was followed by hydrolysis and acetylation to the phospha-glucuronates **43**/**44** (*Scheme 4*). Transesterification to **45**/**46**, selective deacetylation to **48**/**49**, and formation of the trichloroacetimidates **50**/**51** were followed by glycosidation and deprotection to **4**. The tetrazole **5** was prepared from the lactones **54**/**55** *via* the *N*-benzylamides **57**/**58** that were treated with TfN_3 to give the *N*-benzyltetrazoles **59**/**60** (*Scheme 4*). These were transformed into the trichloroacetimidates **63**/**64**, glycosylated to **65**, and deprotected. The *O*-carbamoyl-hydroximo-lactone **7** derived from the glucuronate **67**/**68**, and the phosphonate analogue **8** were prepared by established methods. The phosphonate **4** is slowly hydrolyzed by the *E. coli* β-glucuronidase, but neither **4** nor the tetrazole **5** are affected by the bovine liver β-glucuronidase (*Table 4*). The phenylcarbamate **7** of D-glucarhydroximo-1,5-lactone, but not its phosphonate analogue **8**, is an inhibitor ($K_I = 8$ μM) of the *E. coli* β-glucuronidase. The bovine liver β-glucuronidase is inhibited strongly by **7** ($IC_{50} = 0.2$ μM) and weakly by **8** ($IC_{50} = 2$ mM).

Introduction. – Several glycuronidases play prominent roles. Hyaluronidases (EC 3.2.1.35–36), glucuronidases (EC 3.2.1.31) and iduronidases (EC 3.2.1.76) catalyse the hydrolysis of glycosaminoglycans; their impaired production or activity causes severe lysosomal storage diseases [1]. Polygalacturonidase (EC 3.2.1.15) and other pectinases are involved in the ripening and softening of fruits [2], and large amounts of these enzymes are used for the degradation of cell walls in the production of fruit juice, coffee and tea [3]. Antibody-glucuronidase fusion proteins are used in combination with glycosylated chemotherapeutics for the selective attack on cancer cells [4] [5].

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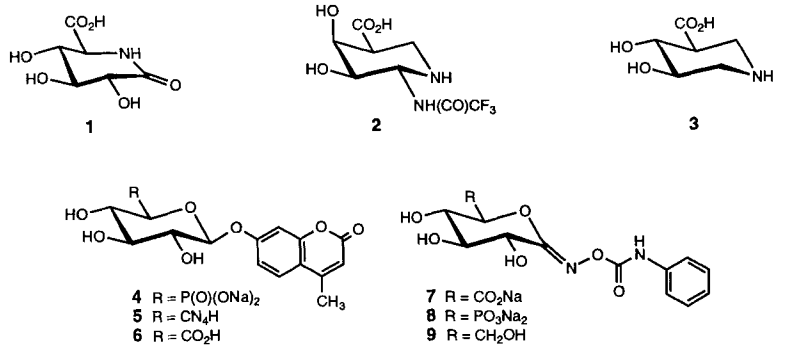
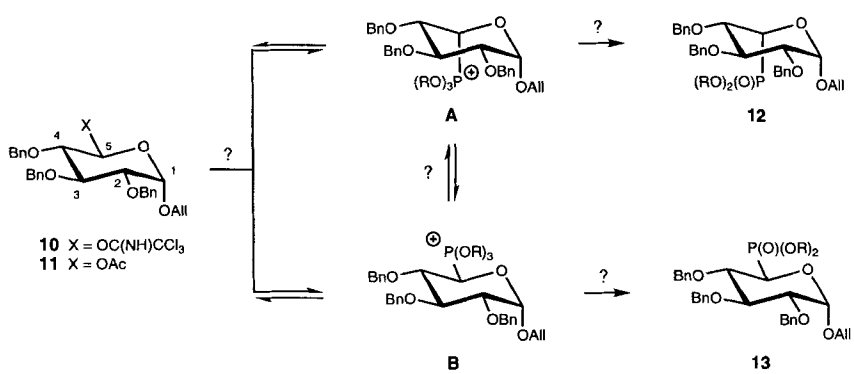
The optimal application of these enzymes requires a control of their activity by inhibitors or, in the case of the cleavage of prodrugs, by tailor-made substrates with a high affinity to the enzyme. A few selective inhibitors of β-glucuronidases are known, such as the lactam **1** [6], the siastatin B analogue **2** [7] and the isofagomine analogue **3** [8][4]).



We wondered if the phosphono analogue **4** and the tetrazolyl analogue **5** of the carboxylic acid **6** are substrates, and if the hydroximo-lactone derived phenylcarbamate **7** and its phosphono analogue **8** are inhibitors of β-glucuronidases[5]). The phenylcarbamate **9** of D-gluconhydroximo-1,5-lactone is indeed a good inhibitor of several β-glucosidases [14] [15], and the phosphonate analogue of *N*-acetyl-2-deoxy-neuraminic acid inhibits *Vibrio cholerae N*-acetyl neuraminidase [16].

Glycosyl phosphonates have been prepared by the *Lewis*-acid-promoted reaction of glycosyl acetates or trichloroacetimidates with phosphites [17–20]. Similarly, hemiacetal derivatives obtained by cleavage of the C(5)–C(6) bond of hexosides should lead to phospha-hexuronic acids (phosphono analogues of hexuronic acids; *Scheme 1*). We wondered about the influence of the configuration at C(1) of precursors such as **10** and **11** on the diastereoselectivity of this substitution. The synthesis of glycosyl phosphonates

Scheme 1



[4]) For other inhibitors of β-glucuronidases, see [6] [9–11].

[5]) Biological activities of phosphonates [12] and tetrazoles [13] have been reviewed.

under mild conditions is kinetically controlled by the favourable *cis*-interaction of the P-center and the vicinal alkoxy group in the intermediate phosphonium salts [19]. The influence, however, of a 1,3-diaxial interaction between the phosphonium substituent and an alkoxy group, as it is realized in the intermediate **A** (*Scheme 1*), is not known; a stabilizing 1,3-interaction should favour **A** over **B**, and lead preferentially to **12**[6]).

We report on the synthesis of the phosphonate **4** and the tetrazole **5**, analogues of the 4-methylumbelliferyl glucuronide (= (4-methylumbelliferyl glucosid)uronic acid; **6**), and their evaluation as substrates of several β-glucuronidases. We also describe the synthesis of the L-*ido*-, D-*gluco*-, and D-*galacto*-configurated phosphonate analogues **12**, **13**, **21**, **22**, **34** and **35** of protected glycuronates, the synthesis of the phenylcarbamate **7** and its phosphono analogue **8**, and their evaluation as inhibitors of the *E. coli* and bovine liver β-glucuronidases.

Results and Discussion. – 1. *Synthesis of the 4-Methylumbelliferyl β-*D*-Glucuronides* **4** *and* **5**. 1.1. L-ido-, D-gluco-, *and* D-galacto-*Configurated Phospha-glycuronates* **12**, **13**, **21**, **22**, **34** *and* **35**. The trichloroacetimidate **10** and the acetate **11** (*Scheme 2*), required for the phosphorylation [17], were prepared from allyl α-D-glucopyranoside (**14**) [21] by tritylation to **15**, benzylation to the crystalline **16**, and detritylation by Et_3SiH in the presence of $BF_3 \cdot OEt_2$. The alcohol **17**, obtained in an overall yield of 71% (*cf.* [22]), was oxidized in the presence of 'BuOH [23] to give the ester **18**. Treatment of **18** with HCO_2H led to the acid **19** (*cf.* [24]). Oxidative decarboxylation with $Pb(OAc)_4$ [25] [26] gave the equatorial acetate **11**[7]) (46% from **17**), avoiding the 1,3-diaxial interaction with the allyloxy group. Not surprisingly [26], treatment of **11** with NaOMe or NH_3 in MeOH failed to give the hemiacetal **20** while reduction with diisobutylaluminium hydride (DIBAH) [27] led exclusively to the equatorial hemiacetal **20** that was converted to the trichloroacetimidate **10** using 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) [28].

Treatment of **10** with $(MeO)_3P$ and trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) in MeCN gave a 1:1 mixture of the L-*ido*/D-*gluco*-configurated **12**/**13** (43% from **11**). Exploratory experiments showed that the analogous treatment in THF or CH_2Cl_2 leads exclusively to **12**. The dependence of the diastereoselectivity in the formation of **12**/**13** on the solvent is in keeping with the known participation of nitriles in glycosidations [29], and a preferred axial attack [30] of MeCN and $(RO)_3P$ on the intermediate oxycarbenium cation. The exclusive formation of **12** in non-participating solvents evidences that the 1,3-diaxial interaction does not interfere with the stabilizing 1,2-*cis*-interaction in the intermediate phosphonium salt; most probably both are stabilizing.

The acetate **11** proved inert to $(MeO)_3P$ and Me_3SiOTf in MeCN. It reacted, however, with $(PhO)_3P$ (Me_3SiOTf, MeCN) to yield 53% of the L-*ido*-anomers **21**/**22** (2:3).

Although, in glycosidations, trichloroacetimidates are more reactive than glycosyl acetates, and although trialkyl phosphites are more nucleophilic than triaryl phosphites [31], the Me_3SiOTf-promoted conversion of the trichloroacetimidate **10** with $(MeO)_3P$ was considerably slower than the conversion of the acetate **11** with $(PhO)_3P$. Hence, the

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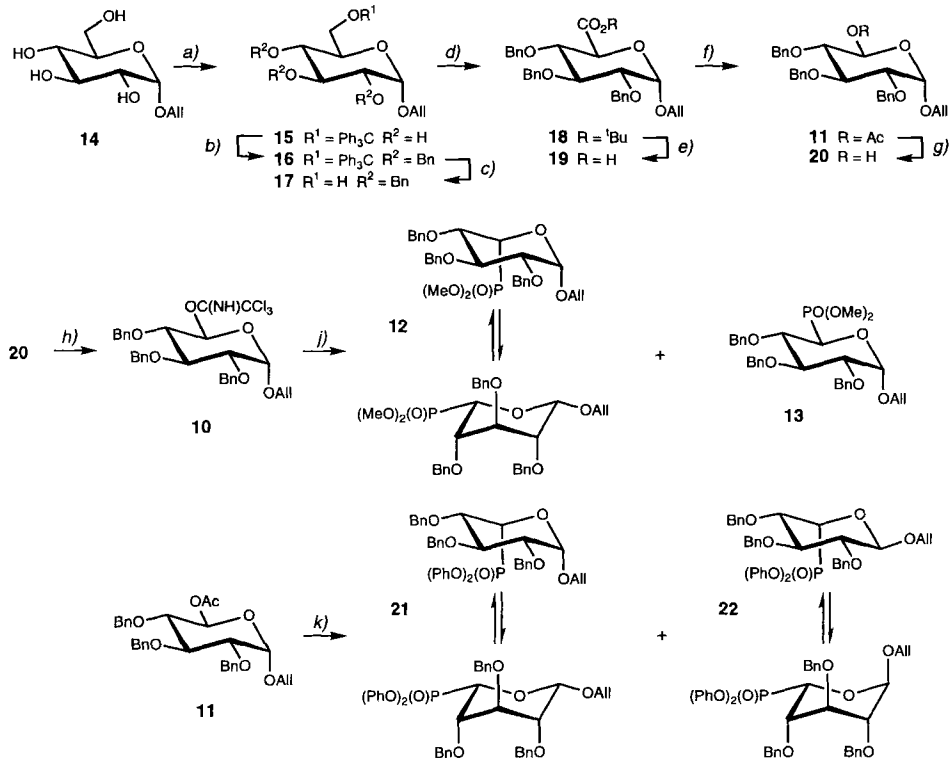
[6]) A stabilizing 1,4-interaction has been postulated in the synthesis of the phosphonic-acid analogue of *N*-acetyl-2,3-didehydro-2-deoxyneuraminic acid [20].

[7]) The ^{1}H-NMR spectrum of crude **11** shows H–C(5) *d*'s at 5.93 (J = 8.3 Hz) and 6.20 ppm (J = 1.4 Hz) and two AcO *s*'s at 2.04 and 2.12 ppm, both in a ratio of *ca.* 20:1.

Scheme 2



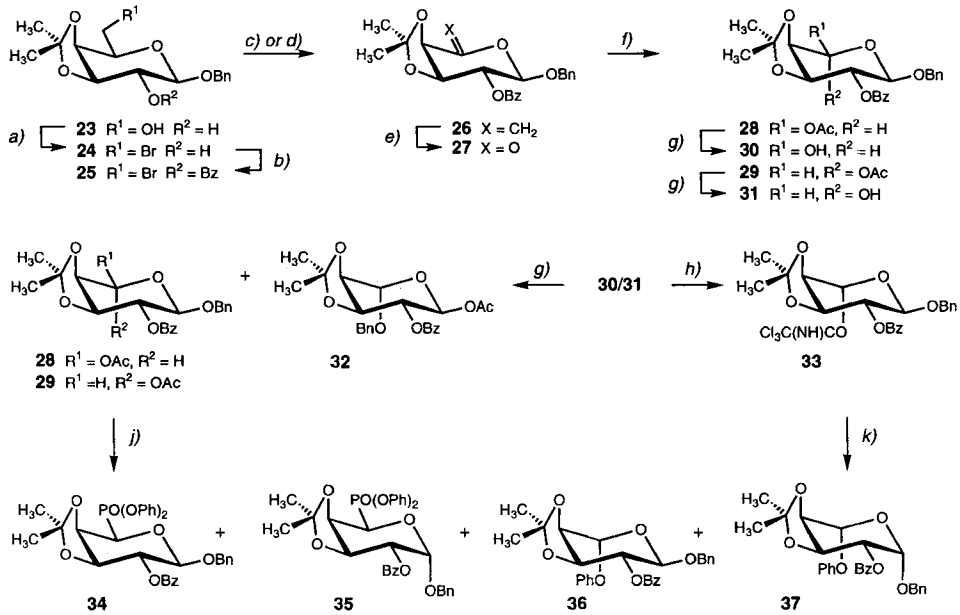
a) Ph_3CCl, Py, 22°; 90%. *b*) BnBr, NaH, Bu_4NI, THF, reflux; 85%. *c*) $BF_3 \cdot OEt_2$, Et_3SiH, $MeCN/CH_2Cl_2$, 0°; 93%. *d*) CrO_3, Py, ᵗBuOH, Ac_2O, CH_2Cl_2/DMF, 23°; 66%. *e*) HCO_2H, 23°; 99%. *f*) $Pb(OAc)_4$, C_6H_6/Py, 60°; 71%. *g*) DIBAH, THF, −78°. *h*) Cl_3CCN, MTBD, $(CH_2)_2Cl_2$, −30°; 87%. *j*) $(MeO)_3P$, Me_3SiOTf, MeCN, 4°; 22% of **12** and 21% of **13** (from **11**). *k*) $(PhO)_3P$, Me_3SiOTf, MeCN, 4°; 33% of **21** and 20% of **22** (from **11**).

different reactivity and stereoselectivity must be due to a different mechanism of the *Arbuzov* rearrangement, resulting in a faster dephenylation. *Arbuzov* has shown the feasibility of an S_NAr reaction of (methyl)triphenoxyphosphonium iodide [32]. However, the conditions of this dephenylation were harsh, suggesting that the rapid dephenylation in the synthesis of **21**/**22** has to be explained otherwise. A plausible mechanism involves attack of a nucleophile such as $AcOSiMe_3$ on the phosphonium center followed by desilylation (→ Me_3SiOTf), transfer of the acetyl group on PhOH, contained to an extent of 5–10% even in distilled $(PhO)_3P$, and loss of PhOH or $PhOSiMe_3$. $(MeO)_3P$ does not contain appreciable amounts of MeOH. Attack of $AcNHSiMe_3$ on the trimethoxy phosphonium salt should be less productive due to the poorer leaving group property of methoxide and the lower concentration of acid. TfOH, formed from PhOH and Me_3SiOTf, must be responsible for the anomerization to **22**, either before or after the formation of **21**.

The phospha-galacturonates **34** and **35** (*Scheme 3*) were prepared from the known galactoside **23** [33]. Bromination of **23** to **24**, followed by benzoylation to **25** and

elimination gave the 5-hexenopyranoside **26**. Ozonolysis led to the lactone **27** which was treated with DIBAH for ten days at −20° in the presence of Ac_2O to give the diastereoisomeric acetates **28**/**29** (52% from **23**) and a minor amount of the hemiacetals **30**/**31** (5% from **23**). Quenching the reaction after 18 h gave only **30**/**31** (42% from **23**). Acetylation of **30**/**31** with Ac_2O/pyridine yielded 87% of **28**/**29** and 7% of the regioisomer **32**[8]), which was the main product of the acetylation at higher temperatures.

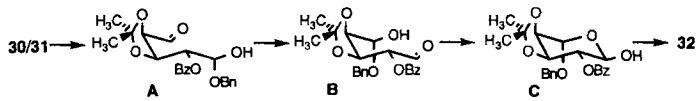
Scheme 3



a) *N*-Bromosuccinimide (NBS), PPh_3, hexamethylphosphoric triamide (HMPA), 80°; 73%. *b*) BzCl, Py, 70°; 98%. *c*) MTBD, HMPA, 70°; 98%. *d*) Bu_4NF, Py, THF, reflux; 80%. *e*) O_3, CH_2Cl_2, −70°, Me_2S; 83%. *f*) DIBAH, THF, Ac_2O, −80° → −20°; 89% of **28**/**29** and 8% of **30**/**31**. *g*) Ac_2O, Py, CH_2Cl_2, −60° → 20°; 87% of **28**/**29** and 7% of **32**. *h*) Cl_3CCN, MTBD, $Cl(CH_2)_2Cl$, −30°. *j*) $P(OPh)_3$, Me_3SiOTf, 1,2-dimethoxyethane/Et_2O, 4°; 44% of **34**, 7% of **35**, 28% of **36** and 14% of **37** (from **28**/**29**). *k*) $P(OPh)_3$, Me_3SiOTf, 1,2-dimethoxyethane, 4°; 35% of **34** and 18% of **35** (from **33**).

The hemiacetals **30**/**31** were also transformed into the labile trichloroacetimidate **33**. Treatment of either the acetates **28**/**29** or the trichloroacetimidate **33** with $(PhO)_3P$ and Me_3SiOTf yielded 51–53% of the phosphonates **34**/**35** (6:1 from **28**/**29**, 2:1 from **33**). The phenyl acetals **36**/**37** (42%, 2:1) were obtained as by-products of the phosphorylation of the acetates **28**/**29**. The diastereoselective formation of the equatorial phosphonates

[8]) Presumably **32** formed by ring opening of **30**/**31**, followed by an intramolecular OBn transfer, leading from the hemiacetal-aldehyde **A** to its isomer **B**, ring closure to **C** and acetylation.



34/35 and the axial acetals **36/37** evidences the preferred axial attack of the nucleophiles which is followed by equilibration of the phosphonium salt. This leads to the equatorial phosphonium salt that is stabilized by interaction with the C(4) benzyloxy group. Similarly as observed for **11**, treatment of **28/29** and **33** with $(PhO)_3P$ and Me_3SiOTf led to anomerization.

The ^{31}P-NMR chemical shift (*Table 1*) and the coupling constants (*Table 2*) of the dimethyl phosphonate **13** evidence a $^4C_1$ conformation, while **12** exists in a conformational equilibrium with an important contribution of the $^1C_4$ conformer, as evidenced by the W-couplings ^4J(P,H–C(3)) = 4.6 and ^4J(H–C(2),H–C(4)) = 0.5, and the coupling constant ^3J(P,H–C(4)) = 10.2, expected for dihedral angles of *ca.* 120° [34]. Similarly, **21** and **22** exist as mixtures of conformers with a decreasing proportion of the $^1C_4$ conformer. The value of ^4J(P,H–C(3)) decreases from **12** to **21** and **22**, and those of ^3J(P,H–C(4)) increase, up to 20.6 Hz for **22** which exists mostly as the $^4C_1$ conformer. The growing tendency of **12**, **21** and **22** to adopt a $^4C_1$ conformation is reflected in the values of ^1J(P–C(5)) (*Table 3*; see [19] and ref. cit. therein). They are smallest for **22** and largest for **12**, in line with the finding that the ^1J(P,C) coupling is larger for equatorial phosphonates than for axial ones [35] [36]. This is also reflected in the ^3J(P,C(3)) and ^3J(P,C(1)) coupling constants. The conformational equilibria of **12**, **21** and **22** indicate that the $-P(O)(OPh)_2$ group may possess a smaller A-value than the $-P(O)(OMe)_2$ group (1.99 kcal/mol [37]).

The assignment of the configuration at C(5) of **28/29** is in keeping with the specific rotations (–59.1° for the axial **29**, –6.4° for the equatorial **28**) and the relative chemical shift of H–C(1) and H–C(5) which both resonate at a slightly lower field for **29** ($\Delta\delta$ = 0.10 and 0.04 ppm, resp.). The small $\Delta\delta$ values indicate that the ring conformation of **28/29** deviates from $^4C_1$, as known for 3,4-di-*O*-isopropylidene-galactopyranoses [38]. The assignment of

Table 1. *Selected ^{1}H-NMR* (300 MHz, $CDCl_3$) *and ^{31}P-NMR* (121 MHz, $CDCl_3$) *Chemical Shifts* δ [ppm] *of the Phosphonates* **8**, **12**, **13**, **21**, **22**, **34**, **35**, **40–48**, **50**, **52**, **53** *and* **78–82**[a])

	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(5)	P
12[b])	4.74	3.49	3.90	3.76	4.33	22.96[c])
13[b])	4.81	3.55	3.99	3.81	4.05	24.60[c])
21[d])	4.91	3.53	4.27	3.94	4.80	13.84
22[d])	5.44	3.62	4.42	4.01	4.88	13.83
34[e])	4.51	5.38	4.34	4.59	4.39	8.84[f])
35[e])	5.25	5.26	4.58	4.66	4.83	11.32[f])
40	6.01	4.55	5.42	4.69	4.41	16.34
41	6.00	4.58	5.41	4.72	4.62	13.54
42[b])	6.03	4.49	5.41	4.85	5.77	10.59[c])
43	6.45	5.15	5.51	5.66	4.45	9.36
44	5.76	5.21	5.32	5.66	4.21	7.90
45	6.32	4.95	5.32–5.44		4.24	17.53
46	5.64	5.08	5.22	5.40	3.94	15.92
47	5.69	5.13	5.26	5.50	4.06	12.20
48[b])	5.44	4.72	5.50	5.27	4.47	20.45
50	6.55	5.00	5.53	5.42	4.37	17.03
52[b])	5.08	5.24	5.30	5.44	4.00	16.01
53[g])	5.14	3.50–3.58		3.83	4.11	22.82
4[h])	5.00		3.58–3.72			13.34
78[b])[d])	7.62	6.15	6.21	6.04	4.54	23.01
79[b])[d])	6.82	6.73	n.d.[i])	n.d.[i])	4.46	22.30
80		5.82[d])	5.51[d])	5.85[d])	4.75[d])	15.53
81		5.74[d])	5.63[d])	5.35[d])	5.87[d])	18.37
82		5.87[d])	5.53[d])	5.86[d])	4.74[d])	14.66
8[e])[h])		4.54	4.17	4.07	3.89	–2.63[j])

[a]) For other signals, see *Exper. Part.* [b]) At 500 MHz. [c]) At 203 MHz. [d]) In C_6H_6. [e]) At 400 MHz. [f]) At 80 MHz. [g]) In CD_3OD. [h]) In D_2O. [i]) Not determined. [j]) At 162 MHz.

Table 2. *Selected ^{1}H-NMR* (300 MHz, $CDCl_3$) *Coupling Constants* J [Hz] *of the Phosphonates* **8**, **12**, **13**, **21**, **22**, **34**, **35**, **40**–**48**, **50**, **52**, **53** *and* **78**–**82**[a])

	J(1,2)	J(2,3)	J(3,4)	J(4,5)	J(P,5)	J(P,4)	J(P,3)	others
12[b])	2.2	5.0	4.0	3.7	14.6	10.2	4.6	J(2,4) = 0.5
13[b])	3.6	9.6	8.8	10.5	9.8	8.8	[c])	
21[d])	2.2	6.0	5.0	4.6	12.7	15.7	3.8	
22[d])	6.2	7.3	7.1	5.7	12.5	20.6	1.2	J(P,1) = 1.2
34[e])	7.6	7.2	5.1	2.2	17.2	[c])	[c])	
35[e])	3.6	7.2	5.3	2.5	16.4	[c])	[c])	
40	3.7	[c])	3.0	9.3	3.2	9.3	[c])	J(P,2) = 2.2
41	3.6	[c])	3.0	5.6	9.0	5.6	[c])	
42[b])	3.6	0.5	2.9	10.1	6.2	8.9	0.5	J(P,2) = 2.2
43	3.6	10.2	10.9	10.9	9.2	9.0	[c])	
44	8.1	9.3	8.9	10.6	10.4	8.9	[c])	
45	3.6	10.1	10.1	9.9	9.9	n.d.[f])	[c])	
46	8.0	10.7	9.2	10.6	10.6	10.6	[c])	
47	8.1	9.4	9.1	10.5	10.5	10.6	0.9	
48[b])	3.4	10.2	9.1	10.7	8.8	11.3	[c])	
50	3.5	10.0	9.3	10.1	10.1	10.7	[c])	
52[b])	7.7	9.5	9.0	10.8	10.8	10.5	0.7	
53[g])	*m*	*m*	*m*	10.4	10.4	n.d.[f])	[c])	
4[h])	6.9	*m*	*m*	*m*	n.d.[f])	n.d.[f])	[c])	
78[b][d])	5.4	4.8	4.8	9.6	10.7	6.3	[c])	
79[b][d])	5.9	5.7	n.d.[f])	n.d.[f])	8.5	6.6	n.d.[f])	
80		4.6	4.4	10.1	8.7	12.2	[c])	
81		1.8	3.4	10.1	7.0	8.8	0.9	J(P,2) = 1.6
82		4.6	4.1	9.4	9.9	9.9	[c])	
8[e][h])		7.9	8.4	7.5	7.5	7.8	[c])	

[a]) For other signals, see *Exper. Part.* [b]) At 500 MHz. [c]) Not observed. [d]) In C_6D_6. [e]) At 400 MHz. [f]) Not determined. [g]) In CD_3OD. [h]) In D_2O.

Table 3. *Selected ^{13}C-NMR* (75 MHz, $CDCl_3$) *Chemical Shifts* δ [ppm] *and ^{13}C,^{31}P-NMR* (75 MHz, $CDCl_3$) *Coupling Constants* J [Hz] *of the Phosphonates* **8**, **12**, **13**, **21**, **22**, **34**, **35**, **40**, **42**–**48**, **50**, **52**, **53**, **78** *and* **80**–**82**[a])

	C(1)	C(2)	C(3)	C(4)	C(5)	J(P,C(5))	J(P,C(3))	J(P,C(1))
12[b])	99.20	75.09[c])	74.37	74.52[c])	71.40	169.3	7.7	10.6
13[b])	96.40	79.35[c])	82.01	78.40[c])	65.86	175.1	17.9	15.0
21[d])	99.71	77.17[c])	75.95	75.92[c])	71.91	168.4	6.3	9.2
22[d])	100.89	79.71[c])	78.28	76.98[c])	68.87	166.8	5.4	6.5
34[e])	100.17	72.70	76.78	72.62	68.83	175.8	15.5	17.5
35[e])	96.14	71.65	73.34	72.60	63.98	177.6	12.1	13.9
40	105.31	77.62[c])	76.57	82.62[c])	65.11	167.7	10.2	[f])
42[b])	105.65	76.85[c])	74.75	82.71[c])	64.43	171.8	10.9	[f])
43	88.93	68.85[c])	69.71	67.22[c])	65.72	177.1	18.2	15.2
44	92.53	69.84[c])	72.84	67.23[c])	68.93	176.0	20.3	18.5
45	88.97	68.88[c])	69.22	67.23[c])	68.93	175.3	17.6	15.0
46	92.60	69.93[c])	72.86	67.70[c])	69.93	173.1	19.7	19.1
47	92.53	69.96[c])	72.81	67.12[c])	69.01	175.3	20.1	19.4
48[b])	90.47	70.97	70.03	68.20	63.87	176.5	18.0	14.9
50	92.77	69.43[c])	69.63	67.27[c])	66.94	174.7	17.9	14.8
52[b])	99.64	70.63[c])	72.69	67.54[c])	69.63	174.9	19.9	18.7
53[g])	102.39	74.28[c])	78.11	71.66[c])	72.89	173.2	20.7	20.1
4[h])	103.82	75.34[c])	78.60	73.20[c])	74.90	156.9	18.0	17.4
78[b][d])	146.33	70.73[c])	71.71	69.01[c])	67.84	162.3	13.6	[f])
80	147.22	66.71[c])	71.35	68.19[c])	71.54	173.5	13.2	11.7
81	154.34	72.27[c])	71.95	80.65[c])	63.67	169.7	10.3	[f])
82	150.86	66.29[c])	70.67	67.99[c])	72.27	173.2	11.5	7.2
8[h][i])	163.13	72.63[c])	77.47	71.66[c])	81.65	143.7	11.6	8.5

[a]) For other signals, see *Exper. Part.* ^2J(P,C(4)) were observed for **13** (2.7 Hz), **34** (5.2 Hz), **35** (5.4 Hz) and **48** (2.5 Hz); ^4J(P,C(2)) was observed for **13** (1.0 Hz). [b]) At 125 MHz. [c]) Signals might be reversed. [d]) In C_6D_6. [e]) At 100 MHz. [f]) Not observed. [g]) In CD_3OD. [h]) In D_2O. [i]) At 50 MHz.

the configuration of **29** and **31–33** is in line with negative NOE's between H–C(3) or H–C(1), and H–C(5). In contrast to the corresponding chemical shifts for **28/29**, H–C(1) of **32** resonates at lower field than H–C(5), unambiguously assigned by ^3J(H–C(4),H–C(5)) = 1.9 Hz.

The large ^1J(P,C(5)) (175.8 and 177.6 Hz) for **34** and **35** point to an equatorial diphenyloxyphosphoryl group [19] [35] [36]. This is confirmed by ^3J(P,C(3)) and ^3J(P,C(1)) of 15.5 and 17.5 Hz (**34**), and 12.1 and 13.9 Hz (**35**), indicating a dihedral angle of *ca.* 180° [39]. The anomeric configuration is demonstrated by ^1J(H–C(1),H–C(2)) of 7.6 Hz (**34**) and 3.6 Hz (**35**) and by the relative chemical shifts of H–C(3) and H–C(5) (*Table 1*). Irradiation of H–C(3) of **36**, but not of **37** leads to an enhancement (2.5%) of the H–C(1) signal, evidencing the configuration at C(1). The H–C(5) signals of **36/37** are not influenced. The axial position of the phenoxy group is evidenced by the relative chemical shifts of H–C(5) and H–C(1) for **34/35** and **36/37** (for **34/35**: $\Delta\delta$ (H–C(5)) = 0.44; $\Delta\delta$ (H–C(1)) = 0.74; for **36/37**: $\Delta\delta$ (H–C(5)) = –0.24; $\Delta\delta$ (H–C(1)) = 0.33).

1.2. *The Phospha Analogue* **4** *and the Tetrazole Analogue* **5** *of 4-Methylumbelliferyl β-*D*-Glucuronide* (**6**). The synthesis of **13** from **14** required nine steps and proceeded in an overall yield of 7%. We, therefore, planned to introduce the phosphono group into a pentodialdose furanoside derivative, following established procedures for the modification at C(5) of monosaccharides [40–42] (*Scheme 4*). The aldehyde **39** [43], readily available by periodate cleavage of the diol **38** [44], reacted with $HP(O)(OPh)_2$ in the presence of *Hünig*'s base to yield the α-hydroxyphosphonates **40** and **41** (49%; 3:1)[9]. The D-*gluco*-configuration of the major isomer **40** was established by X-ray analysis of its diacetate **42** (*Fig. 1*). Treatment of the mixture **40/41** with aqueous CF_3CO_2H or with aqueous HCO_2H solution, followed by acetylation, gave the D-*gluco*-phosphonates **43/44** (67%; 3:2). The L-*ido*-isomer was not observed. A one-pot procedure starting with 60 g of **38** yielded 19.8 g of **43/44** (16%; 3:2).

Transesterification of **43/44** with $BnOH/Ti(O^iPr)_4$ [45] led to the hemiacetals **48/49** (35%). Treatment of the diphenyl esters **43/44** with BnOH, KF and [18]crown-6 [46] gave mostly the dibenzyl esters **45/46** (58%; 3:2) besides the mixed ester **47** (2%) and the hemiacetals **48/49** (9%). The dibenzyl esters **45/46** were selectively deacetylated with $(NH_4)_2CO_3$ in DMF [47] to yield 86% of **48/49** (7:1). Cl_3CCN in the presence of K_2CO_3 gave mostly the unexpected [48] α-D-anomer **50** (87%; **50/51** 7:1). $BF_3 \cdot OEt_2$-Promoted glycosidation of **50/51** with 4-methyl-*O*-(trimethylsilyl)umbelliferone [49] led to the phospha-glucuronide **52** (30%). Deacetylation of **52** to **53** (99%), hydrogenation and ion-exchange gave the sodium phosphonate **4** (91% from **52**).

The tetrazole **5** was synthesized from the glucuronolactones **54/55** in nine steps and in an overall yield of 7% (*Scheme 4*). Thus, **54/55** reacted with excess $BnNH_2$ to the crystalline glycosylamine **56** (57%), that was hydrolyzed and acetylated to the *N*-benzyl amides **57/58** (48%; 3:2). Treating **57/58** with NaN_3/Tf_2O and *Hünig*'s base in MeCN [50] yielded 61% of the anomeric tetrazoles **59/60** (3:2). Selective deacetylation of **59/60** with $(NH_4)_2CO_3$ in DMF [47] and treatment of the resulting hemiacetals **61/62** (71%; 15:1) with Cl_3CCN and NaH gave the trichloroacetimidates **63/64** (75%; α/β 3:2). Glycosidation of **63/64** with 4-methyl-*O*-(trimethylsilyl)umbelliferone yielded 75% of the β-D-glycoside **65**, while the acetates **59/60** did not react even in the presence of 5 equiv. of Me_3SiOTf in boiling CH_2Cl_2. Transesterification of **65** to the crystalline triol **66** (76%), followed by hydrogenolysis gave **5** (98%).

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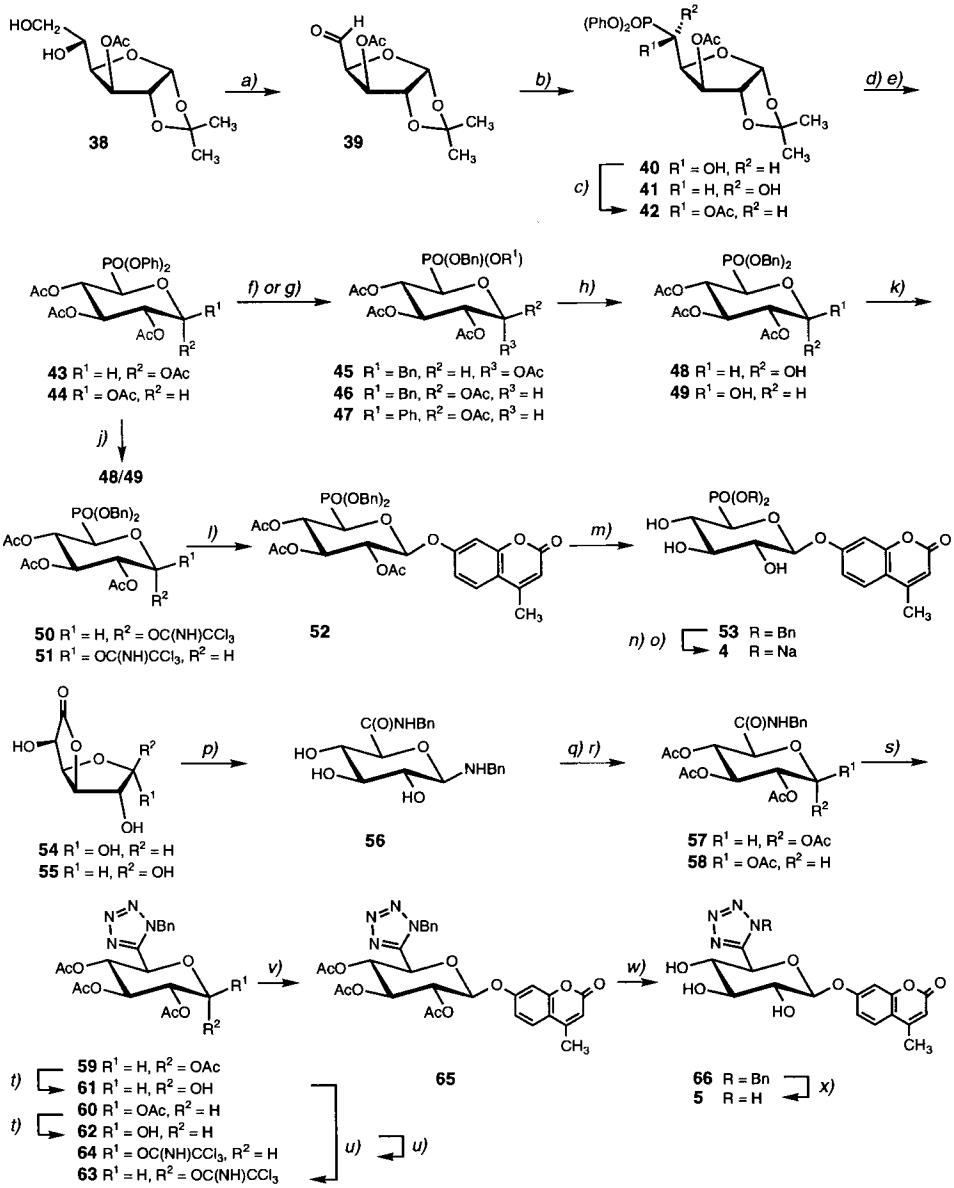
[9]) The mixture cannot be stored at room temperature for more than a month and is labile to SiO_2. On a small scale, **40** and **41** were separated by HPLC.

Scheme 4



a) $NaIO_4$, H_2O, 22–30°. *b*) $HP(O)(OPh)_2$, $^iPr_2EtN$, CH_2Cl_2, 22–30°; 49% from **38**. *c*) Ac_2O, Py, CH_2Cl_2, 23°; 86%. *d*) HCO_2H, AcOEt, H_2O, 90 min. *e*) Ac_2O, $HClO_4$ or Py; 67% from **40**/**41**, 16–48% from **38**. *f*) BnOH, KF, [18]crown-6, THF, 23°; 58% of **45**/**46**, 2% of **47** and 9% of **48**/**49**. *g*) BnOH, KF, [18]crown-6, THF, 23°, Ac_2O, Py, 23°; 44% of **45**/**46**. *h*) $(NH_4)_2CO_3$, DMF, 23°; 86%. *j*) $Ti(O^iPr)_4$, BnOH, 60°; 35%. *k*) Cl_3CCN, CH_2Cl_2, K_2CO_3, 21°; 87%. *l*) 4-Methyl-7-(trimethylsilyl)umbelliferone, $BF_3 \cdot Et_2O$, CH_2Cl_2, −20° → 23°, Ac_2O, Py, −20° → 23°; 30%. *m*) NH_3, MeOH, 0° → 23°. *n*) HCO_2H, 10% Pd/C, MeOH, 23°. *o*) *Dowex® 50W X2* (50–100 mesh, Na^+ form); 91% from **52**. *p*) $BnNH_2$, H_2O, 0°; 57%. *q*) *Amberlite IR-120* (H^+-form). *r*) Ac_2O, Py, 23°; 57%. *s*) Tf_2O, NaN_3, $^iPr_2EtN$, MeCN, 25°; 61%. *t*) $(NH_4)_2CO_3$, DMF, 25°; 71%. *u*) Cl_3CCN, NaH, CH_2Cl_2, 21°; 75%. *v*) 4-Methyl-7-*O*-(trimethylsilyl)umbelliferone, $BF_3 \cdot Et_2O$, CH_2Cl_2, −20° to 21°; 75%. *w*) NaOMe, MeOH, 25°; 76%. *x*) HCO_2H, 10% Pd/C, MeOH, 23°; 98%.

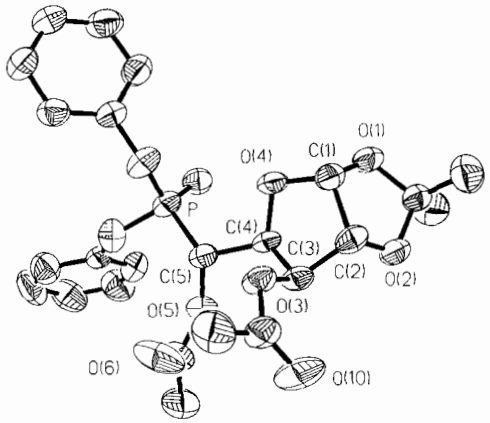


Fig. 1. *ORTEP Representation of* **42**

The conformation of **42** in the solid state corresponds to the one in solution as evidenced particularly by the coupling constant ^3J(H–C(4),H–C(5)) = 10.1 Hz and the corresponding P–C(5)–C(4)–C(3) angle of 166° [51]. The solution conformation of **40** is very similar to the one of **42** (^3J(H–C(4),H–C(5)) = 9.3 Hz). Both conformations deviate only slightly from the one found in the crystal structure of (5*R*)-5-*C*-(diethoxyphosphoryl)-1,2-*O*-isopropylidene-3-*O*-(methylsulfonyl)-α-D-xylofuranose (P–C(5)–C(4)–C(3) angle of 178°) [52]. The phase angle of pseudorotation *P* is 59.0° (57.9° for the mesylate), characterizing the conformation of **42** as E_4 [53]. The amplitude of puckering τ_m is 40.8° (41.4° for the mesylate). A rarely observed ^5J(P,H–C(2)) of 2.2 Hz was proven by a H,H-correlation and a P-decoupled ^{1}H-NMR spectrum. The large ^3J(H,H) prove the $^4C_1$ pyranose structures of **43**/**44**, and the large ^1J(P,C(5)) evidences the equatorial diphenoxyphosphoryl groups. The coupling constant ^3J(H–C(1),H–C(2)) = 7.7 confirms the expected β-D-configuration of **52**.

The ^{1}H-NMR spectrum ((D$_6$)DMSO) of **56** shows two *AB* spin systems at 3.87 and 4.30 ppm. The ^3J values (8.8–9.3 Hz) of the H–C(1) to H–C(5) signals evidence the formation of a β-D-pyranose. The ^{1}H-NMR spectrum of **57**/**58** shows four AcO *s*'s, and the N*H*CH$_2$ signals at 6.53–6.65 ppm and the NHC*H*$_2$ signals at 4.32–4.52 ppm. The structure of **61** has been established by X-ray analysis (*Fig. 2*). The tetrazole **61** adopts a $^4C_1$ conformation with dihedral angles N(14)–C(6)–C(5)–O(5) of −109° and C(6)–N(11)–C(16)–C(17) of 116.9°. The $^4C_1$ structure of **5** is evidenced by ^3J values for H–C(1) to H–C(5) of 7.7–9.7 Hz.

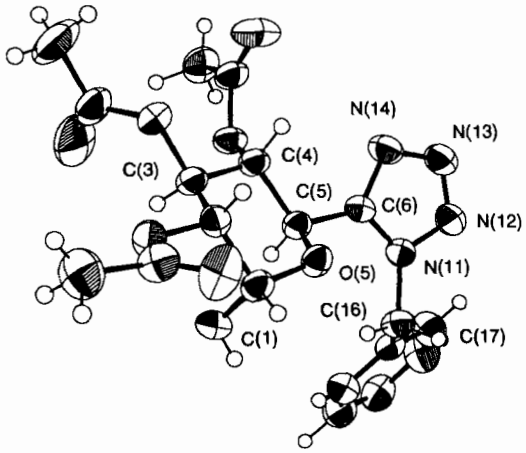
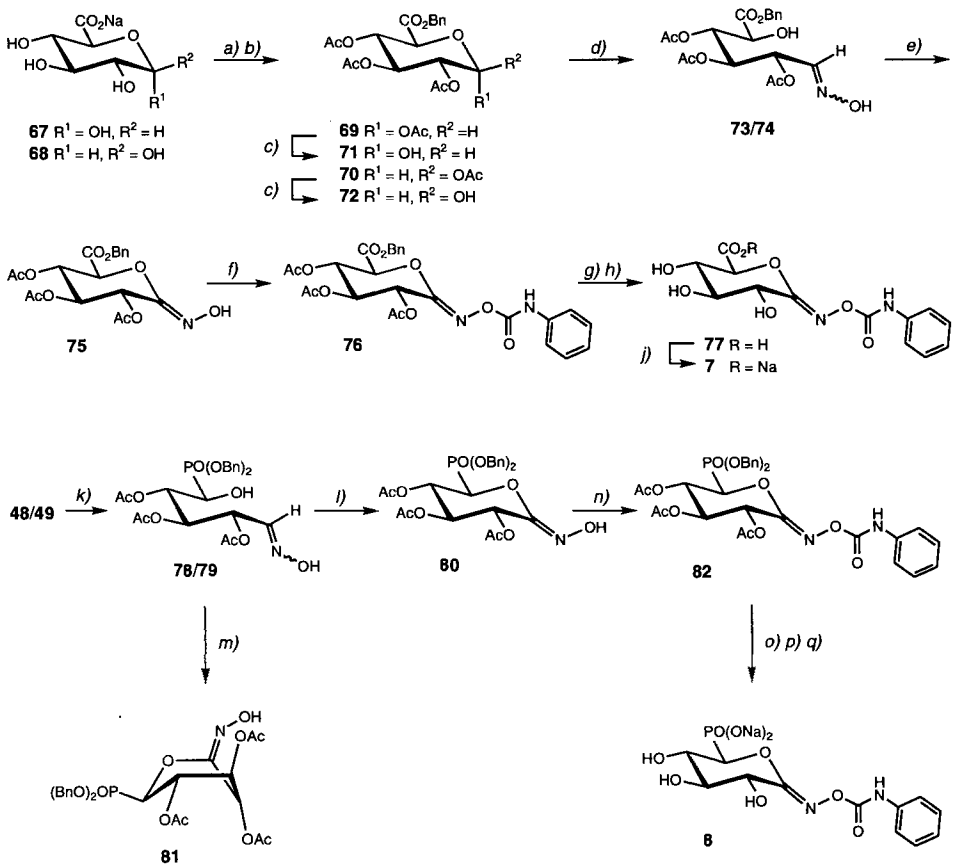


Fig. 2. *ORTEP Representation of* **61**

2. *Synthesis of the Phenylcarbamates* **7** *and* **8**. The carbamate **7** was prepared from sodium D-glucuronate (**67**/**68**) by known methods (*Scheme 5*). Benzylation and acetylation of **67**/**68** gave 49% of the anomeric benzyl esters **69**/**70** (1:1). Selective deacetylation (67%) [47] and oximation of the hemiacetals **71**/**72** gave **73**/**74** ((*E*)/(*Z*) 7:3; *cf.* [54] [55]). Remarkably, $NH_2OH \cdot HCl$ in pyridine hardly affected the ester functions. Oxidation of **73**/**74** with *N*-chlorosuccinimide/1,8-diazabicyclo[5.4.0]undec-7-ene (NCS/DBU) at −78° [54] led to the (*Z*)-hydroximo-lactone **75** (77%), while oxidation at higher temperatures gave (*E*)/(*Z*)-mixtures (*cf.* [55]). Treatment of **75** with PhNCO yielded 77% of the phenylcarbamate **76**. Deprotection by hydrogenolysis and ammonolysis, and filtration through an ion-exchange column gave the sodium carboxylate **7** (86%).

Scheme 5



a) BnBr, DMF, 23°. *b*) Ac_2O, Py, 23°; 49% from **67**/**68**. *c*) $(NH_4)_2CO_3$, DMF, 22°; 67%. *d*) $NH_2OH \cdot HCl$, Py, 23°. *e*) NCS, DBU, CH_2Cl_2, −78° → 23°; 77% from **71**/**72**. *f*) PhNCO, $^iPr_2EtN$, CH_2Cl_2, 0°; 77%. *g*) H_2, 10% Pd/C, MeOH, 23°. *h*) NH_3, MeOH, 22°. *j*) *Dowex® 50W X2* (50–100 mesh, Na^+ form); 86% from **76**. *k*) $NH_2OH \cdot HCl$, Py, 4 h. *l*) NCS, DBU, CH_2Cl_2, −78° → 23°; 88% from **48**/**49**. *m*) NCS, DBU, CH_2Cl_2, 23°; 63% from **48**/**49**. *n*) PhNCO, $^iPr_2EtN$, CH_2Cl_2, 0°; 98%. *o*) H_2, 10% Pd/C, MeOH, 22°. *p*) NH_3, MeOH, 22°. *q*) *Dowex® 50W X2* (50–100 mesh, Na^+ form); 48% from **82**.

Similarly, in the phosphonate series, oximation of the hemiacetals **48**/**49** gave **78**/**79** ((*E*)/(*Z*) 3:1). Oxidation with NCS/DBU [54] starting at −78° led exclusively to the (*Z*)-hydroximo-lactone **80** (88%). Oxidation at −20° gave a 1:1 mixture **80**/**81**, while the (*E*)-configurated **81**, isolated in 63% yield, was the only product at 23°. Conversion of **80** to the phenylcarbamate **82** (98%), and deprotection by hydrogenolysis and ammonolysis gave, after ion exchange, the sodium phosphonate **8** in 48% yield.

The (*E*)/(*Z*)-mixture **73**/**74** is characterised by two C(1) *d*'s at 145.50 and 146.41 ppm, two NOH *s*'s at 8.34 (0.7 H) and 8.55 (0.3 H) ppm, and two H–C(1) *d*'s at 7.29 (0.7 H) and 6.55 (0.3 H) ppm. Similarly, the (*E*)/(*Z*)-mixture **78**/**79** gives rise to C(1) *d*'s at 146.33 ppm and 146.81 ppm. The chemical shift of the C(1) *s*'s of **75** (147.53 ppm) and **80** (147.22 ppm) evidences the (*Z*)-configuration. In agreement with earlier findings [56], C(1) of the (*E*)-configurated **81** resonates at lower field ($\Delta\delta = 7.12$). The ^3J values point to a $^4C_1$ conformation of **75** and **80**, and to a $_5B_2$ conformation of **81**.

3. *Enzymatic Evaluation of the Phospha-glucuronide* **4**, *the Tetrazole* **5**, *and the Phenylcarbamates* **7** *and* **8**. The phosphonate **4**, but not the tetrazole **5**, is slowly hydrolyzed by the *E. coli* β-glucuronidase (*Table 4*). The K_M value of **4** is *ca.* sixty times higher than the K_M value of the corresponding carboxylate **6** [57]. Like 4-nitrophenyl β-D-glucuronamide [58], the phosphonate **4** and the tetrazole **5** are not hydrolyzed by the bovine liver β-glucuronidase.

Table 4. K_I *and* K_M *Values for Inhibitors and Substrate Analogues of β-Glucuronidases*

Compound	D-Glucaro-1,4-lactone	**1**	**2**	**3**	**4**
Source	bovine liver	bovine liver	bovine liver	bovine liver	*E. coli*
Substrate[a])	4-NPGUA	4-NPGUA	?	?	
pH	5.2	5.2	?	5	7.2
K_I [μM]	0.46	0.039	0.029	0.079	
K_M [μM]	356	356			9900
K_M/K_I	774	9130			
Reference	[6] [9]	[6]	[7]	[8]	[57]

Compound	**4**	**5**	**6**	**7**	**8**
Source	bovine liver	bovine liver	*E. coli*	*E. coli*	*E. coli*
Substrate[a])				4-NPGUA	4-NPGUA
pH	4.5	4.5	7.2	7.2	7.2
K_I [μM]				8	> 8000
K_M [μM]	no activity at 70 μmol	no activity at 70 μmol	170	1600	1600
K_M/K_I				200	< 0.2
Reference			[57]		

[a]) 4-NPGUA = (4-nitrophenyl β-D-glucopyranosid)uronic acid.

The phenylcarbamate **7** of D-glucarhydroximo-1,5-lactone is quite a strong inhibitor of the *E. coli* ($K_I = 8$ μmol) and the bovine liver β-glucuronidases ($IC_{50} = 0.2$ μmol). As evidenced by a comparison of the K_M/K_I ratios, **7** is a slightly stronger inhibitor than the *gluco*-configurated pipecolic acid ($K_M/K_I = 46$) [10], about as strong as D-glucaro-1,4-lactone [6], but fourty times weaker than the lactam **1** [6]. The phosphonate analogue **8** does not show any inhibition of the *E. coli* up to 8 mM, but a very weak inhibition of the bovine liver β-glucuronidase ($IC_{50} = 2$ mM).

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Experimental Part

General. Moisture sensitive reactions were run under Ar or N_2 in dry solvents. TLC: *Merck* silica gel *60* F_{254} plates; detection by heating with I_2 soln./20% H_2SO_4 1:1 (I_2 soln.: 10 g of I_2, 100 g of KI, 1000 ml of H_2O) or with vanillin soln. (5%) in H_2SO_4. Flash chromatography (FC): silica gel (*Fluka* or *Merck 60*; 0.040–0.063 mm). HPLC: *Spherisorb*® SiO_2 (5 μm) column (20 × 250 mm); detection at 254 nm; flow 16 ml/min. M.p.: uncorrected. UV: λ_{max} ($\log\varepsilon$) in nm. NMR Spectra: Me_4Si (^1H and ^{13}C) and H_3PO_4 (^{31}P) as external references, and HDO (^1H in D_2O and CD_3OD) as internal reference; chemical shifts δ in ppm and coupling constants J in Hz. MS: 3-NOBA = 3-nitrobenzyl alcohol.

Allyl 6-O-Trityl-α-D-glucopyranoside (**15**). A soln. of **14** [21][10]) (12.5 g, 56.8 mmol) and Ph_3CCl (20.0 g, 71.7 mmol) in pyridine (120 ml) was stirred at *ca.* 23° for 12 h and at 60° for 1 h. After the addition of Ph_3CCl (12.0 g, 43.0 mmol), the soln. was stirred at 60° until all starting material had disappeared (*ca.* 3.5 h). The warm soln. was treated with H_2O (120 ml), cooled, and extracted with AcOEt. The combined org. layers were washed with 1M H_2SO_4 and brine. Evaporation and FC (400 g of SiO_2, toluene/acetone 2:1 → 1:1) gave **15** (23.3 g, 90%). Grey glassy solid. R_f (toluene/acetone 1:1) 0.18. IR ($CHCl_3$): 3568*s*, 3443*s*, 3088*m*, 3063*m*, 3008*s*, 2930*s*, 2881*m*, 1960*w*, 1821*w*, 1599*m*, 1491*s*, 1449*s*, 1406*m*, 1334*m*, 1145*s*, 1045*s*, 1003*s*, 934*m*, 900*m*. ^1H-NMR (300 MHz, CD_3OD): 3.20 (*dd*, J = 9.9, 6.7, H–C(6)); 3.22 (*dd*, J = 10.1, 8.8, H–C(4)); 3.39 (*dd*, J = 9.9, 1.9, H′–C(6)); 3.43 (*dd*, J = 9.7, 3.8, H–C(2)); 3.63 (*dd*, J = 9.7, 8.8, H–C(3)); 3.81 (*ddd*, $J \approx$ 9.8, 6.8, 1.7, H–C(5)); 4.15 (*ddt*, J = 12.9, 6.2, 1.4, 1 allyl. H); 4.37 (*ddt*, J = 12.9, 5.3, 1.5, 1 allyl. H); 4.90 (*d*, J = 3.8, H–C(1)); 5.21 (*dq*, J = 10.3, 1.8, 1 olef. H); 5.38 (*dq*, J = 17.3, 1.7, 1 olef. H); 6.07 (*dddd*, J = 17.3, 10.3, 6.2, 5.3, 1 olef. H); 7.18–7.31 (*m*, 9 arom. H); 7.44–7.48 (*m*, 6 arom. H). ^{13}C-NMR (50 MHz, CD_3OD): 64.15 (*t*); 68.64 (*t*); 70.94 (*d*); 71.64 (*d*); 72.29 (*d*); 74.83 (*d*); 87.07 (*s*); 97.45 (*d*); 118.45 (*t*); 127.43–129.09 (several *d*); 134.19 (*d*); 144.30 (3*s*). CI-MS (NH_3): 462 (2), 405 (2), 404 (6), 386 (3), 385 (14), 260 (3), 259 (10), 245 (9), 244 (63), 243 (100), 183 (7), 182 (2), 167 (4), 165 (4), 105 (2), 35 (2).

Allyl 2,3,4-Tri-O-benzyl-6-O-trityl-α-D-glucopyranoside (**16**). A soln. of **15** (15.9 g, 34.3 mmol) in THF[11]) (390 ml) was treated with a suspension of NaH (6.9 g, *ca.* 150 mmol) at *ca.* 23° for 10 min followed by the addition of BnBr (25.0 ml, 211 mmol) and Bu_4NI (1.9 g, 5.1 mmol). The soln. was heated to reflux until TLC indicated completion of the reaction (*ca.* 24 h), treated with Et_2O, and filtered through SiO_2. Evaporation and FC (600 g of SiO_2, Et_2O/hexane 1:9 → Et_2O) gave **16** (21.4 g, 85%). Colourless crystals. M.p. 94.0–95.5° (EtOH/MeOH). R_f (hexane/AcOEt 4:1) 0.36. $[\alpha]_D^{25} = +49.9$ (c = 1.26, $CHCl_3$). IR ($CHCl_3$): 3088*m*, 3065*s*, 3008*s*, 2928*s*, 2876*s*, 1953*w*, 1876*w*, 1811*w*, 1598*m*, 1492*s*, 1450*s*, 1359*s*, 1328*m*, 1159*s*, 1071*s*, 1028*s*, 933*m*, 900*m*. ^1H-NMR (300 MHz, C_6D_6): 3.42 (*dd*, J = 9.9, 5.0, H–C(6)); 3.66 (*dd*, J = 10.0, 1.8, H′–C(6)); 3.69 (*dd*, J = 9.7, 3.6, H–C(2)); 3.78 (*t*, $J \approx$ 9.5, H–C(4)); 3.95 (*ddt*, J = 13.1, 5.9, 1.4, 1 allyl. H); 4.12 (*ddd*, $J \approx$ 10.3, 4.7, 1.4, H–C(5)); 4.24 (*ddt*, J = 13.1, 5.1, 1.5, 1 allyl. H); 4.27 (*t*, $J \approx$ 9.3, H–C(3)); 4.40 (*d*, J = 11.3), 4.85 (*d*, J = 11.0, PhCH_2); 4.49 (*d*, J = 11.9), 4.55 (*d*, J = 12.1, PhCH_2); 4.78 (*d*, J = 11.3), 5.00 (*d*, $J \approx$ 10.1, PhCH_2); 5.02 (*d*, $J \approx$ 3.3, H–C(1)); 5.07 (*dq*, J = 10.4, 1.3, 1 olef. H); 5.37 (*dq*, J = 17.2, 1.7, 1 olef. H); 5.90 (*dddd*, J = 17.2, 10.4, 5.9, 5.1, 1 olef. H); 6.69–7.17 (*m*, 18 arom. H); 7.30–7.35 (*m*, 4 arom. H); 7.64–7.68 (*m*, 8 arom. H). ^{13}C-NMR (75 MHz, C_6D_6): 63.46 (*t*); 68.49 (*t*); 71.33 (*d*); 72.96 (*t*); 75.12 (*t*); 75.74 (*t*); 78.93 (*d*); 81.40 (*d*); 82.85 (*d*); 86.95 (*s*); 96.44 (*d*); 117.21 (*t*); 127.29–129.32 (several *d*); 134.73 (*d*); 139.11 (*s*); 139.32 (*s*); 139.89 (*s*); 144.78 (3*s*). FAB-MS (3-NOBA): 731 (1, $[M-1]^+$), 244 (33), 243 (100), 91 (75). Anal. calc. for $C_{49}H_{48}O_6$ (732.91): C 80.30, H 6.60; found: C 80.14, H 6.51.

Allyl 2,3,4-Tri-O-benzyl-α-D-glucopyranoside (**17**). A soln. of $BF_3 \cdot OEt_2$ (5.0 ml, 39.8 mmol) in MeCN (90 ml) was added dropwise to a cooled (0°) soln. of **16** (13.4 g, 18.3 mmol) and Et_3SiH (14.5 ml, 91.5 mmol) in CH_2Cl_2 (150 ml). After stirring for 10 min and the addition of sat. aq. $NaHCO_3$ soln. (100 ml) and H_2O (200 ml), the mixture was shaken vigorously. The aq. layer was extracted with CH_2Cl_2, and the combined org. layers were washed with brine, dried ($MgSO_4$), and evaporated. FC (400 g of SiO_2, AcOEt/hexane 1:5 → 1:1) afforded **17** (8.35 g, 93%). R_f (hexane/AcOEt 2:1) 0.20. IR ($CHCl_3$): 3595*s*, 3089*m*, 3066*m*, 3008*s*, 2926*s*, 2876*s*, 1952*w*, 1875*w*, 1811*w*, 1604*w*, 1497*m*, 1455*s*, 1360*s*, 1157*s*, 1070*s*, 1028*s*, 934*m*. ^1H-NMR (300 MHz, C_6H_6): 1.48 (br. *s*, exchange with CD_3OD, HO–C(6)); 3.48 (*dd*, J = 9.6, 3.5, H–C(2)); 3.63 (*dd*, J = 9.8, 8.9, H–C(4)); 3.72–3.85 (*m*, H–C(5), 2 H–C(6), 1 allyl. H; addition of CD_3OD → 3.75 (*dd*, $J \approx$ 11.9, 4.3, H–C(6)), 3.78 (*dd*, $J \approx$ 11.2, 3.5, H′–C(6)), 3.85 (*ddt*, J = 13.1, 6.0, 1.4, 1 allyl. H)); 4.09 (*ddt*, J = 13.1, 4.3, 1.5, 1 allyl. H); 4.23 (*t*, J = 9.2, H–C(3)); 4.48 (*d*, J = 12.1), 4.57 (*d*, J = 11.9, PhCH_2); 4.65 (*d*, J = 11.3), 4.91 (*d*, J = 11.2, PhCH_2); 4.77 (*d*, J = 3.5, H–C(1)); 4.80 (*d*, J = 11.5), 5.00 (*d*, J = 11.7, PhCH_2); 5.03 (*dq*, J = 10.5, 1.5, 1 olef. H); 5.28 (*dq*, J = 17.2, 1.7, 1 olef. H); 5.81

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[10]) ^{13}C-NMR (50 MHz, CD_3OD): 62.83 (*t*); 69.54 (*t*); 72.07 (*d*); 73.77 (*d*); 74.02 (*d*); 75.36 (*d*); 99.50 (*d*); 117.87 (*t*); 135.97 (*d*).

[11]) Similar conditions, but using DMF, resulted in a 20% lower yield.

(*dddd*, J = 17.2, 10.5, 6.0, 5.1, 1 olef. H); 7.05–7.35 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, C_6D_6): 62.17 (*t*); 68.52 (*t*); 71.84 (*d*); 73.01 (*t*); 75.16 (*t*); 75.63 (*t*); 78.21 (*d*); 80.98 (*d*); 82.28 (*d*); 96.60 (*d*); 117.16 (*t*); 127.58–128.64 (several *d*); 134.54 (*d*); 139.22 (2*s*); 139.81 (*s*). CI-MS (NH_3): 509 (28), 508 (86, $[M + NH_4]^+$), 451 (17), 450 (57), 399 (24), 341 (32), 253 (48), 235 (24), 187 (19), 181 (26), 179 (26), 175 (15), 108 (49), 91 (100).

tert-*Butyl (Allyl 2,3,4-Tri-*O*-benzyl-*α*-*D*-glucopyranosid)uronate* (**18**). A suspension of CrO_3 (6.8 g, 6.8 mmol) in DMF/CH_2Cl_2 4:1 (180 ml) was treated with pyridine (11.0 ml, 142 mmol), stirred vigorously at *ca.* 23° for 30 min, treated with a soln. of **17** (8.35 g, 17.0 mmol) in DMF/CH_2Cl_2 4:1 (45 ml), treated with Ac_2O (13.0 ml, 11.8 mmol) and ^{t}BuOH (34.0 ml, 362 mmol), stirred for 9 h, treated with MeOH (30 ml), stirred for 30 min, concentrated to ¼ of its volume, and diluted with Et_2O (250 ml). Filtration through Na_2SO_4 and SiO_2 (300 g), elution with Et_2O, evaporation, and FC (330 g of SiO_2, hexane/AcOEt 9:1) gave **18** (6.30 g, 66%). R_f (hexane/AcOEt 2:1) 0.63. $[\alpha]_D^{25} = +14.1$ (c = 1.37, $CHCl_3$). IR ($CHCl_3$): 3089*w*, 3067*w*, 3008*m*, 2983*w*, 2933*w*, 2873*w*, 1952*w*, 1875*w*, 1811*w*, 1735*s*, 1497*w*, 1455*m*, 1394*m*, 1370*s*, 1159*s*, 1070*s*, 1048*s*, 1029*s*, 998*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.49 (*s*, Me_3C); 3.61 (*dd*, J = 8.6, 2.6, H–C(2)); 3.78 (*dd*, J = 9.9, 9.1, H–C(4)); 4.04 (*t*, $J \approx$ 9.3, H–C(3)); 4.06 (*ddt*, $J \approx$ 11.9, 6.7, 1.2, 1 allyl. H); 4.15 (*d*, J = 10.0, H–C(5)); 4.22 (*ddt*, J = 12.8, 5.2, 1.5, 1 allyl. H); 4.67 (*d*, $J \approx$ 11.9), 4.88 (*d*, J = 10.6, PhCH_2); 4.83 (*d*, $J \approx$ 10.9), 4.95 (*d*, J = 10.9, PhCH_2); 4.48 (*d*, $J \approx$ 3.7, H–C(1)); 5.26 (*dq*, J = 10.3, 1.6, 1 olef. H); 5.38 (*dq*, J = 17.2, 1.5, 1 olef. H); 5.98 (*dddd*, J = 17.2, 10.3, 6.7, 5.2, 1 olef. H); 7.23–7.39 (*m*, 15 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 27.94 (3*q*); 68.69 (*t*); 71.44 (*d*); 73.43 (*t*); 75.09 (*t*); 75.89 (*t*); 79.51 (*d*); 79.73 (*d*); 81.45 (*d*); 82.12 (*s*); 96.78 (*d*); 118.83 (*t*); 127.66–128.50 (several *d*); 133.56 (*d*); 138.06 (*s*); 138.21 (*s*); 138.69 (*s*); 168.84 (*s*). CI-MS (NH_3): 578 (5, $[M + NH_4]^+$), 464 (8), 413 (8), 339 (5), 253 (14), 197 (5), 187 (7), 181 (8), 179 (6), 147 (6), 131 (6), 108 (39), 106 (15), 105 (34), 92 (15), 91 (100), 78 (9), 77 (6), 58 (6), 41 (5), 35 (15). Anal. calc. for $C_{34}H_{40}O_7$ (560.69): C 72.83, H 7.19; found: C 72.96, H7.22.

*(Allyl 2,3,4-Tri-*O*-benzyl-*α*-*D*-glucopyranosid)uronic Acid* (**19**). A soln. of **18** (6.25 g, 11.1 mmol) in HCO_2H (150 ml) was stirred at *ca.* 23° for 30 min. Evaporation yielded chromatographically pure **19** (5.60 g, 99%). R_f (AcOEt/hexane/HCO_2H 1:1:trace) 0.47. IR ($CHCl_3$): 3089*m*, 3067*s*, 3008*s*, 2931*s*, 2874*s*, 1952*w*, 1875*w*, 1729*s*, 1603*w*, 1497*m*, 1455*s*, 1360*m*, 1267*m*, 1156*s*, 1071*s*, 1028*s*, 998*s*, 936*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.59 (*dd*, J = 9.7, 3.6, H–C(2)); 3.72 (*t*, $J \approx$ 9.5, H–C(3)); 4.02 (br. *dd*, $J \approx$ 12.7, 6.7, 1 allyl. H); 4.06 (*t*, $J \approx$ 9.2, H–C(4)); 4.19 (br. *dd*, $J \approx$ 12.8, 5.2, 1 allyl. H); 4.29 (*d*, J = 10.0, H–C(5)); 4.64 (*d*, J = 12.0), 4.78 (*d*, J = 12.0, PhCH_2); 4.65 (*d*, J = 10.5), 4.84 (*d*, J = 10.3, PhCH_2); 4.82 (*d*, $J \approx$ 10.7), 4.99 (*d*, J = 10.9, PhCH_2); 4.84 (*d*, $J \approx$ 3.5, H–C(1)); 5.25 (br. *dq*, $J \approx$ 10.3, 1.0, 1 olef. H); 5.33 (br. *dq*, J = 17.2, 1.5, 1 olef. H); 5.92 (*dddd*, J = 17.2, 10.3, 6.7, 5.2, 1 olef. H); 7.22–7.34 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 68.88 (*t*); 69.86 (*d*); 73.40 (*t*); 75.33 (*t*); 75.06 (*t*); 79.14 (*d*); 79.26 (*d*); 81.42 (*d*); 96.13 (*d*); 118.90 (*t*); 127.77–128.55 (several *d*); 133.18 (*d*); 137.47 (*s*); 137.84 (*s*); 138.46 (*s*); 174.18 (*s*). CI-MS (NH_3): 524 (9), 523 (34), 522 (100, $[M + H]^+$), 464 (27), 414 (13), 413 (48), 355 (19), 339 (12), 253 (21), 203 (9), 181 (14), 179 (10), 108 (41), 105 (26), 92 (10), 91 (79), 35 (14).

*Allyl (5*R*)-5-*C*-Acetoxy-2,3,4-tri-*O*-benzyl-*α*-*D*-xylopyranoside* (**11**). A soln. of **19** (5.60 g, 11.1 mmol) in C_6H_6/pyridine 10:1 (55 ml) was treated with $Pb(OAc)_4$ (16.80 g, *ca.* 32 mmol) at 60° for 25 min. Filtration through SiO_2, elution with Et_2O, evaporation, and FC (300 g of SiO_2, AcOEt/hexane 1:6) gave **11** (4.1 g, 71%). R_f (hexane/AcOEt 4:1) 0.29. $[\alpha]_D^{25} = +37.9$ (c = 0.51, $CHCl_3$). IR ($CHCl_3$): 3089*w*, 3067*w*, 3008*w*, 2933*w*, 2874*w*, 1759*s*, 1497*w*, 1455*m*, 1367*m*, 1248*w*, 1161*m*, 1070*s*, 1028*s*, 937*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.04 (*s*, AcO); 3.54 (br. *t*, $J \approx$ 8.4, H–C(4)); 3.59 (*dd*, J = 9.6, 3.6, H–C(2)); 4.06 (*t*, J = 9.4, H–C(3)); 4.10 (*ddt*, J = 12.8, 6.8, 1.1, 1 allyl. H); 4.38 (*ddt*, J = 12.8, 5.2, 1.4, 1 allyl. H); 4.65 (*d*, J = 12.1), 4.79 (*d*, J = 11.9, PhCH_2); 4.73 (*d*, J = 11.5), 4.82 (*d*, J = 11.5, PhCH_2); 4.77 (*d*, $J \approx$ 3.4, H–C(1)); 4.84 (*d*, J = 10.7), 4.95 (*d*, J = 10.8, PhCH_2); 5.26 (*dq*, J = 10.3, 1.1, 1 olef. H); 5.37 (*dq*, J = 17.2, 1.5, 1 olef. H); 5.93 (*d*, J = 8.3, H–C(5)); 5.96 (*dddd*, J = 17.2, 10.3, 6.8, 5.2, 1 olef. H); 7.24–7.37 (*m*, 15 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 21.16 (*q*); 68.78 (*t*); 73.67 (*t*); 75.47 (*t*); 76.33 (*t*); 79.50 (*d*); 80.54 (*d*); 81.37 (*d*); 90.18 (*d*); 95.35 (*d*); 119.09 (*t*); 128.05–128.84 (several *d*); 133.68 (*d*); 138.36 (*s*); 138.63 (*s*); 139.01 (*s*); 169.75 (*s*). FAB-MS (3-NOBA): 518 (2), 517 (7, $[M - 1]^+$), 459 (2), 311 (4), 181 (26), 175 (12), 154 (10), 136 (12), 131 (14), 107 (12), 105 (11), 92 (26), 91 (100), 77 (10), 71 (16). Anal. calc. for $C_{31}H_{34}O_7$ (518.60): C 71.80, H 6.61; found: C 71.73, H 6.49.

*Allyl (5*S*)-2,3,4-Tri-*O*-benzyl-5-*C*-hydroxy-*α*-*D*-xylopyranoside* (**20**). A soln. of **11** (553 mg, 0.96 mmol) in CH_2Cl_2 (20 ml) was treated with 20% DIBAH in toluene (2.8 ml, *ca.* 2.9 mmol) at −78°, stirred for 15 min, and treated with a sat. NH_4Cl soln. (2 ml). The mixture was allowed to warm to *ca.* 23°, diluted with H_2O and 1M H_2SO_4 (10 ml), and shaken. The aq. layer was extracted with CH_2Cl_2 (3 ×), and the combined org. layers were washed with brine (2 ×), dried ($MgSO_4$), and evaporated to yield **20** (499 mg, 98%) which was used without further purification for the next step. R_f (hexane/AcOEt 2:1) 0.32. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.92 (br. *s*, OH); 3.33 (*dd*, J = 9.2, 7.8, H–C(4)); 3.60 (*dd*, J = 9.7, 3.7, H–C(2)); 3.99 (*t*, J = 9.5, H–C(3)); 4.07 (*ddt*, J = 12.9, 6.6, 1.2, 1 allyl. H); 4.23 (*ddt*, J = 12.9, 5.2, 1.4, 1 allyl. H); 4.65 (*d*, J = 12.0), 4.79 (*d*, J = 12.0, PhCH_2); 4.78 (*d*, J = 3.7, H–C(1)); 4.81 (*d*, $J \approx$ 11.2), 4.89 (*d*, $J \approx$ 11.9, PhCH_2); 4.85 (*d*, J = 10.9), 4.93 (*d*, J = 10.9, PhCH_2); 5.06 (*d*,

J = 7.8, H–C(5)); 5.24 (*dq*, J = 10.3, 1.5, 1 olef. H); 5.34 (*dq*, J = 17.2, 1.5, 1 olef. H); 5.93 (*dddd*, J = 17.1, 10.3, 6.6, 5.2, 1 olef. H); 7.28–7.42 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 68.62 (*t*); 73.40 (*t*); 75.06 (*t*); 75.95 (*t*); 79.39 (*d*); 79.91 (*d*); 83.60 (*d*); 92.50 (*d*); 95.22 (*d*); 118.44 (*t*); 127.65–128.45 (several *d*); 133.53 (*d*); 138.09 (*s*); 138.39 (*s*); 138.74 (*s*).

Allyl (5R)-2,3,4-Tri-O-benzyl-5-C-(trichloroacetimidoyloxy)-α-D-xylopyranoside (**10**). A soln. of crude **20** (200 mg, *ca.* 0.42 mmol) in $Cl(CH_2)_2Cl/Cl_3CCN$ 10:1 (6.6 ml) was treated with 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD; 66 µl, 0.46 mmol) at −30°, stirred for 10 min, and filtered through SiO_2. Elution with Et_2O and evaporation gave crude **10** which was sufficiently pure (^{1}H-NMR, TLC) to be used for the next step. R_f (hexane/AcOEt 1:2) 0.53. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.67 (*dd*, J = 9.6, 3.6, H–C(2)); 3.72 (*dd*, $J \approx$ 9.0, 8.4, H–C(4)); 4.10 (*t*, $J \approx$ 9.3, H–C(3)); 4.15 (*ddt*, J = 12.7, 6.7, 1.1, 1 allyl. H); 4.49 (*ddt*, J = 12.7, 5.2, 1.4, 1 allyl. H); 4.67 (*d*, J = 12.1), 4.82 (*d*, J = 12.1, PhCH_2); 4.79 (*d*, J = 10.7), 4.93 (*d*, J = 10.7, PhCH_2); 4.86 (*d*, J = 3.6, H–C(1)); 4.87 (*d*, J = 10.9), 4.95 (*d*, J = 10.9, PhCH_2); 5.27 (*dq*, J = 10.3, 1.1, 1 olef. H); 5.38 (*dq*, J = 17.2, 1.6, 1 olef. H); 6.00 (*dddd*, J = 17.1, 10.3, 6.7, 5.2, 1 olef. H); 6.15 (*d*, J = 8.2, H–C(5)); 7.28–7.41 (*m*, 15 arom. H); 8.73 (*s*, NH). ^{13}C-NMR (75 MHz, $CDCl_3$): 68.75 (*t*); 73.45 (*t*); 75.22 (*t*); 76.03 (*t*); 78.99 (*d*); 80.11 (*d*); 81.10 (*d*); 94.32 (*d*); 95.35 (*d*); 118.63 (*t*); 127.66–128.50 (several *d*); 133.47 (*d*); 138.01 (2*s*); 138.66 (*s*); 161.14 (*s*).

Allyl (5S)-2,3,4-Tri-O-benzyl-5-C-(dimethoxyphosphoryl)-α-D-xylopyranoside (**12**) *and Allyl (5R)-2,3,4-Tri-O-benzyl-5-C-(dimethoxyphosphoryl)-α-D-xylopyranoside* (**13**). A soln. of crude **10** (350 mg) in MeCN (6 ml) was treated with $P(OMe)_3$ (240 µl, 1.26 mmol) and Me_3SiOTf (83 µl, 0.46 mmol) at −17°, allowed to warm to 4°, stirred for 3 h, and filtered through SiO_2. Elution with Et_2O, evaporation, and FC (22 g of SiO_2, hexane/AcOEt 1:1) gave **12**/**13** (147 mg, 62% from **11**) which was separated by HPLC (hexane/AcOEt 1:2): **12** (52 mg, 22% from **11**) and **13** (49 mg, 21% from **11**).

Data of **12**: R_f (hexane/AcOEt 2:3) 0.21. IR ($CHCl_3$): 3088*w*, 3067*w*, 3007*m*, 2957*w*, 2856*w*, 1603*w*, 1497*w*, 1455*m*, 1363*w*, 1317*w*, 1142*m*, 1073*s*, 1041*s*, 934*m*, 829*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Tables 1* and *2*; 3.68 (*d*, J = 10.9, MeO); 3.79 (*d*, J = 10.7, MeO); 4.10 (*ddt*, J = 13.2, 6.6, 1.3, 1 allyl. H); 4.46 (*ddt*, J = 13.2, 4.8, 1.6, 1 allyl. H); 4.48 (*s*, PhCH_2); 4.60 (*d*, J = 11.4), 4.66 (*d*, J = 11.4, PhCH_2); 4.65 (*d*, J = 12.4), 4.77 (*d*, J = 12.4, PhCH_2); 5.20 (*dq*, J = 10.4, 7.2, 1.6, 1 olef. H); 5.95 (*dddd*, J = 17.1, 11.3, 6.6, 4.8, 1 olef. H); 7.17–7.39 (*m*, 15 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 3*; 52.93 (*dq*, J(C,P) = 7.0); 53.69 (*dq*, J(C,P) = 6.3); 70.28 (*t*); 72.73 (*t*); 73.12 (*t*); 73.59 (*t*); 117.55 (*t*); 127.63–128.45 (several *d*); 134.15 (*d*); 137.71 (*s*); 137.90 (*s*); 138.46 (*s*). CI-MS (NH_3): 587 (13), 586 (39, $[M + NH_4]^+$), 570 (8), 569 (26, $[M + 1]^+$), 512 (30), 511 (100), 295 (10), 263 (8), 254 (14), 253 (80), 243 (11), 240 (9), 203 (11), 187 (14), 108 (24), 105 (11), 91 (75). Anal. calc. for $C_{31}H_{37}O_8P$ (568.60): C 65.48, H 6.56; found: C 65.29, H 6.76.

Data of **13**: R_f (hexane/AcOEt 2:3) 0.26. IR ($CHCl_3$): 3090*w*, 3067*w*, 3005*m*, 2956*m*, 2927*m*, 2873*m*, 1604*w*, 1497*w*, 1455*m*, 1360*m*, 1153*m*, 1067*s*, 1037*s*, 948*m*, 912*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Tables 1* and *2*; 3.69 (*d*, J = 10.8, MeO); 3.80 (*d*, J = 10.5, MeO); 4.00 (*ddt*, J = 12.8, 6.6, 1.2, 1 allyl. H); 4.16 (*ddt*, J = 12.8, 5.2, 1.4, 1 allyl. H); 4.62 (*d*, J = 12.1), 4.77 (*d*, J = 12.1, PhCH_2); 4.80 (*d*, $J \approx$ 10.6), 4.89 (*d*, $J \approx$ 10.3, PhCH_2); 4.83 (*d*, $J \approx$ 11.2), 4.97 (*d*, $J \approx$ 10.9, PhCH_2); 5.24 (*dq*, J = 10.3, 1.1, 1 olef. H); 5.33 (*dq*, J = 17.2, 1.6, 1 olef. H); 5.93 (*dddd*, J = 17.1, 10.3, 6.7, 5.2, 1 olef. H); 7.24–7.35 (*m*, 15 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 3*; 52.74 (*dq*, J(P,C) = 6.8); 53.88 (*dq*, J(P,C) = 6.5); 68.73 (*t*); 73.46 (*t*); 75.26 (*t*); 75.90 (*t*); 118.66 (*t*); 127.63–128.49 (several *d*); 133.28 (*d*); 138.00 (*s*); 138.11 (*s*); 138.63 (*s*). Anal. calc. for $C_{31}H_{37}O_8P$ (568.60): C 65.48, H 6.56; found: C 65.22, H 6.68.

Allyl (5S)-2,3,4-Tri-O-benzyl-5-C-(diphenoxyphosphoryl)-α/β-D-xylopyranosides (**21**/**22**). A mixture of **11** (2.30 g, 4.43 mmol), distilled $(PhO)_3P$ (1.28 ml, 4.87 mmol), and 3-Å molecular sieves in MeCN (80 ml) was treated with Me_3SiOTf (0.92 ml, 5.09 mmol) at −20° and stirred at 4° for 1 h. Filtration through *Hyflo Super Cel*®, addition of SiO_2 (40 g), evaporation, and FC (300 g of SiO_2, hexane/AcOEt 5:1 → 5:2) gave **21** (1.00 g, 33%) and **22** (0.60 g, 20%).

Data of **21**: Colourless crystals. M.p. 58.0–59.0° (hexane/AcOEt). R_f (hexane/AcOEt 2:1) 0.56. $[\alpha]_D^{25} = +31.3$ (c = 1.46, $CHCl_3$). IR ($CHCl_3$): 3067*w*, 3007*m*, 2873*w*, 1592*m*, 1491*s*, 1455*m*, 1363*m*, 1310*w*, 1178*m*, 1162*s*, 1075*s*, 1052*s*, 1027*s*, 1009*m*, 997*s*, 936*s*, 904*m*. ^{1}H-NMR (300 MHz, C_6H_6): see *Tables 1* and *2*; 4.04 (*ddt*, J = 13.4, 6.4, 1.3, 1 allyl. H); 4.40 (*d*, J = 11.8), 4.48 (*d*, J = 11.8, PhCH_2); 4.46 (*d*, J = 11.9), 4.55 (*d*, J = 11.8, PhCH_2); 4.49 (*ddt*, J = 13.4, 4.8, 1.7, 1 allyl. H); 4.57 (*d*, J = 11.9), 4.78 (*d*, J = 11.8, PhCH_2); 5.00 (*dq*, J = 10.4, 1.3, 1 olef. H); 5.24 (*dq*, J = 17.3, 1.7, 1 olef. H); 5.83 (*dddd*, J = 17.3, 10.4, 6.4, 4.8, 1 olef. H); 6.73–7.43 (*m*, 25 arom. H). ^{13}C-NMR (125 MHz, C_6D_6): see *Table 3*; 70.82 (*t*); 73.42 (*t*); 73.68 (2*t*); 117.14 (*t*); 121.40 (*d*); 121.44 (*d*); 121.80 (*d*); 121.84 (*d*); 124.81 (*d*); 125.03 (*d*); 127.66–129.80 (several *d*); 134.84 (*d*); 138.50 (*s*); 138.70 (*s*); 139.37 (*s*); 151.47 (*d*, J(P,C) = 9.2); 151.53 (*d*, J(P,C) = 9.0). FAB-MS (3-NOBA): 716 (10), 715 (30, $[M + Na]^+$), 694 (35), 693 (89, $[M + 1]^+$), 692 (12), 691 (41, $[M - 1]^+$), 637 (9), 636 (39), 635 (100), 419 (14), 181 (14). Anal. calc. for $C_{41}H_{41}O_8P$ (692.74): C 71.09, H 5.97, P 4.47; found: C 70.90, H 5.91, P 4.33.

Data of **22**: Colourless crystals. M.p. 70.5–71.5° (hexane/AcOEt). R_f (hexane/AcOEt 2:1) 0.63. $[\alpha]_D^{25} = -43.9$ ($c = 1.27$, $CHCl_3$). IR ($CHCl_3$): 3067*w*, 3007*m*, 2873*w*, 1592*m*, 1491*s*, 1455*m*, 1363*m*, 1310*w*, 1178*m*, 1162*s*, 1075*s*, 1052*s*, 1027*s*, 1009*m*, 997*s*, 936*s*, 904*m*. ^{1}H-NMR (300 MHz, C_6D_6): see *Tables 1* and *2*; 3.94 (*ddt*, $J = 13.1, 5.8, 1.4$, 1 allyl. H); 4.31 (*ddt*, $J = 13.2, 5.0, 1.6$, 1 allyl. H); 4.49 (*d*, $J = 11.5$), 4.63 (*d*, $J \approx 11.7$, PhCH_2); 4.65 (*d*, $J = 11.8$), 4.83 (*d*, $J = 11.5$, PhCH_2); 4.67 (*d*, $J = 12.5$), 4.74 (*d*, $J = 12.6$, PhCH_2); 5.00 (*dq*, $J = 10.5, 1.4$, 1 olef. H); 5.23 (*dq*, $J = 17.2, 1.7$, 1 olef. H); 5.80 (*dddd*, $J = 17.2, 10.5, 5.8, 5.0$, 1 arom. H); 6.74–7.39 (*m*, 25 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 3*; 69.85 (*t*); 73.86 (*t*); 74.00 (*t*); 74.47 (*t*); 117.90 (*t*); 121.10 (*d*); 121.19 (*d*); 121.28 (*d*); 121.36 (*d*); 125.50 (*s*); 125.59 (*s*); 128.05–130.17 (several *d*); 134.08 (*d*); 137.98 (*s*); 138.66 (*s*); 138.66 (*s*); 150.60 (*d*, J(P,C) ≈ 10.0); 150.80 (*d*, J(P,C) ≈ 10.2). FAB-MS (3-NOBA): 694 (3), 693 (7, $[M + 1]^+$), 419 (12), 181 (13), 136 (10), 92 (19), 91 (100). Anal. calc. for $C_{41}H_{41}O_8P$ (692.74): C 71.09, H 5.97, P 4.47; found: C 71.25, H 6.18, P 4.48.

*Benzyl 6-Bromo-6-deoxy-3,4-*O*-isopropylidene-β-*D*-galactopyranoside* (**24**). A soln. of **23**[12]) (28.8 g, 92.90 mmol) in HMPA (72 ml) was treated with Ph_3P (53.4 g, 203.6 mmol) and NBS (36.3 g, 203.9 mmol), stirred at 80° for 30 min, diluted with H_2O (700 ml), and extracted with Et_2O (6 × 700 ml) and AcOEt (10 × 700 ml). Drying of the combined org. layers and evaporation gave a residue (228 g) which was dissolved in AcOEt and treated with hexane to precipitate Ph_3PO. Evaporation of the mother liquor and MPLC (1 kg of SiO_2, hexane/AcOEt 2:1) gave **24** (27.1 g) which was purified further by crystallization (pentane/Et_2O): 25.2 g (73%) of colourless needles. M.p. 85.2–86.2°. R_f (hexane/AcOEt 1:1) 0.68. $[\alpha]_D^{24.5} = -5.3$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3600*m*, 2990*m*, 2940*m*, 2880*m*, 2840*w*, 1495*w*, 1465*w*, 1455*m*, 1385*s*, 1375*s*, 1324*w*, 1295*w*, 1246*s*, 1156*s*, 1146*s*, 1128*s*, 1110*s*, 1070*s*, 1030*s*, 986*m*, 968*m*, 912*w*, 875*s*, 850*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.36, 1.52 (2*s*, 2 Me); 1.56 (*s*, exchange with D_2O, HO–C(2)); 3.58–3.66 (*m*, 2 H–C(6), H–C(2)); 3.91–3.95 (*m*, H–C(5)); 4.07 (*dd*, $J = 7.4, 5.5$, H–C(3)); 4.24 (*d*, $J = 8.3$, H–C(1)); 4.26 (*dd*, $J = 7.4, 5.5$, H–C(4)); 4.65 (*d*, $J = 11.6$), 4.95 (*d*, $J = 11.6$, PhCH_2); 7.26–7.40 (*m*, 5 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 26.26 (*q*); 28.03 (*q*); 29.76 (*t*); 70.80 (*t*); 73.49 (3*d*); 78.66 (*d*); 100.72 (*d*); 110.34 (*s*); 128.16 (*d*); 128.43 (2*d*); 128.55 (2*d*); 136.55 (*s*). CI-MS (C_4H_{10}): 375 (44, $[M + 1]^+$), 373 (46), 357 (11), 355 (12), 299 (25), 297 (23), 267 (100), 265 (98), 237 (8), 235 (9), 175 (24), 91 (46). Anal. calc. for $C_{16}H_{21}BrO_5$ (373.25): C 51.49, H 5.67, Br 21.41; found: C 51.47, H 5.72, Br 21.26.

*Benzyl 2-*O*-Benzoyl-6-bromo-6-deoxy-3,4-*O*-isopropylidene-β-*D*-galactopyranoside* (**25**). A soln. of crystalline **24** (6.01 g, 16.1 mmol) in $CHCl_3$ (49 ml) and pyridine (2.9 ml, 36 mmol) was treated with BzCl (5.08 ml, 43.8 mmol) for 2 h at 70°. Addition of a sat. aq. $NaHCO_3$ soln. (250 ml), extraction with AcOEt (3 × 300 ml), evaporation, and FC (350 g of SiO_2, hexane/AcOEt 1:5) of the residue (12.75 g) gave **25** (7.52 g, 98%). White needles. M.p. 110°. R_f (hexane/AcOEt 1:1) 0.61. $[\alpha]_D^{24.5} = -5.4$ ($c = 0.56$, $CHCl_3$). IR ($CHCl_3$): 2990*m*, 2940*w*, 2880*w*, 1730*s*, 1610*w*, 1495*w*, 1450*m*, 1385*s*, 1375*s*, 1326*w*, 1317*m*, 1270*s*, 1160*m*, 1146*s*, 1131*s*, 1110*s*, 1070*s*, 1028*s*, 1000*m*, 968*m*, 926*w*, 912*w*, 876*w*, 850*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.36, 1.64 (2*s*, 2 Me); 3.66–3.69 (*m*, 2 H–C(6)); 3.98 (*td*, $J = 6.5, 2.0$, H–C(5)); 4.31 (*dd*, $J = 6.7, 5.5$, H–C(3)); 4.34 (*dd*, $J = 2.0, 5.4$, H–C(4)); 4.50 (*d*, $J = 8.1$, H–C(1)); 4.69 (*d*, $J = 12.6$), 4.89 (*d*, $J = 12.6$, PhCH_2); 5.31 (*dd*, $J = 8.2, 6.7$, H–C(2)); 7.21–7.25 (*m*, 5 arom. H); 7.43–7.47 (*m*, 2 arom. H); 7.56–7.61 (*m*, 1 arom. H); 8.01–8.03 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 26.27 (*q*); 27.62 (*q*); 29.65 (*t*); 69.92 (*t*); 73.28 (*d*); 73.32 (*d*); 73.56 (*d*); 77.11 (*d*); 98.59 (*d*); 110.77 (*s*); 127.78 (*d*); 127.91 (2*d*); 128.27 (2*d*); 128.31 (2*d*); 129.86 (1*s*, 2*d*); 133.09 (*d*); 136.77 (*s*); 165.28 (*s*). CI-MS (C_4H_{10}): 371 (100, $[M - C_7H_7O]^+$), 370 (19), 369 (96), 105 (4), 91 (3). Anal. calc. for $C_{23}H_{25}BrO_6$ (477.36): C 57.87, H 5.28, Br 16.74; found: C 57.95, H 5.22, Br 16.76.

*Benzyl 2-*O*-Benzoyl-6-deoxy-3,4-*O*-isopropylidene-α-*L*-arabino-hex-5-enopyranoside* (**26**). a) A soln. of **25** (3.02 g, 6.33 mmol) in HMPA (30 ml) was treated with 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD; 1.1 ml, 7.59 mmol) at 70° for 30 h. The mixture was poured on sat. aq. $NaHCO_3$ soln. (50 ml). Usual workup (Et_2O) and FC (hexane/AcOEt 4:1) followed by crystallization in pentane/Et_2O gave **26** (2.36 g, 94%).

b) A soln. of **25** (12.00 g, 25.14 mmol) in THF (300 ml) was treated with $Bu_4NF \cdot 3\,H_2O$ (19.84 g, 62.88 mmol) and pyridine (60 ml) under reflux for 1.5 h. Usual workup and MPLC (hexane/AcOEt 6:1 → 3:1) followed by crystallization (pentane/Et_2O) gave **26** (7.95 g, 80%). M.p. 112.4–112.7°. R_f (hexane/AcOEt 4:1) 0.28. $[\alpha]_D^{24.5} = -92.1$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3070*w*, 3030*m*, 3010*m*, 2990*m*, 2930*m*, 1730*s*, 1664*m*, 1604*w*, 1496*w*, 1452*s*, 1385*s*, 1374*s*, 1318*s*, 1265*s*, 1240*s*, 1180*s*, 1165*s*, 1112*s*, 1100*s*, 1072*s*, 1030*s*, 992*s*, 875*m*, 860*m*, 710*s*, 770*s*, 668*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.38, 1.54 (2*s*, 2 Me); 4.35 (*dd*, $J = 6.5, 4.5$, H–C(3)); 4.77 (br. *d*, $J = 6.6$, H–C(4)); 4.87 (br. *s*, H′–C(6)); 4.90 (br. *s*, H–C(6)); 4.44 (*d*, $J = 12.2$), 4.90 (*d*, $J = 12.2$, PhCH_2); 4.97 (*d*, $J = 4.3$, H–C(1)); 5.41 (*t*, $J \approx 4.4$, H–C(2)); 7.23–7.33 (*m*, 5 arom. H); 7.43–7.46 (*m*, 2 arom. H); 7.58–7.60 (*m*, 1 arom. H); 8.01–8.03 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 25.67 (*q*); 26.74 (*q*); 69.79 (*t*); 70.41 (*d*); 72.10 (*d*); 74.40 (*d*); 97.78 (*d*); 99.08 (*t*); 110.90 (*s*); 127.80 (*d*); 128.08 (2*d*); 128.30 (2*d*); 128.37 (2*d*); 129.42 (*s*); 129.87 (2*d*);

[12]) M.p. 122.5–123.5° (AcOEt/hexane).

133.34 (*d*); 136.69 (*s*); 152.25 (*s*); 164.95 (*s*). CI-MS (C_4H_9): 397 (13, $[M + 1]^+$), 396 (5), 340 (7), 339 (27), 290 (21), 289 (100), 217 (7), 105 (5), 91 (6), 69 (6). Anal. calc. for $C_{23}H_{24}O_6$ (396.44): C 69.68, H 6.10; found: C 69.61, H 6.20.

(Benzyl 2-O-Benzoyl-3,4-O-isopropylidene-α-L-arabinopyranosid)urono-5,1-lactone (**27**). A soln. of crystalline **26** (8.25 g, 20.81 mmol) in CH_2Cl_2 (600 ml) was treated with O_3 at −78°, stirred for 30 min, treated with Me_2S (1.83 ml, 24.95 mmol), allowed to warm to r.t., and poured on 10% aq. $NaHSO_3$ soln. (600 ml). Usual workup (CH_2Cl_2) gave crude **26** (8.51 g) which was crystallized in AcOEt/pentane: 6.88 g (83%) of colourless needles. M.p. 136.4–137.3°. $[\alpha]_D^{24.5} = -107.4$ ($c = 1.0$, $CHCl_3$). R_f (hexane/AcOEt 1:1) 0.34. IR ($CHCl_3$): 3090*w*, 3070*w*, 3020*m*, 2990*w*, 2940*w*, 1770*s*, 1740*s*, 1732*s*, 1604*w*, 1496*w*, 1454*m*, 1386*s*, 1376*s*, 1318*m*, 1260*s*, 1245*s*, 1180*s*, 1160*s*, 1110*s*, 1094*s*, 1072*s*, 1025*s*, 1000*s*, 974*m*, 930*w*, 915*w*, 862*w*, 705*s*, 664*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.38, 1.49 (2*s*, 2 Me); 4.61 (*dd*, $J = 7.3, 3.7$, H–C(3)); 4.71 (*d*, $J = 12.1$), 4.96 (*d*, $J = 12.1$, PhCH_2); 4.77 (*d*, $J = 7.2$, H–C(4)); 5.45 (*dd*, $J = 5.6, 3.7$, H–C(2)); 5.48 (*d*, $J = 5.6$, H–C(1)); 7.27–7.31 (*m*, 5 arom. H); 7.46–7.49 (*m*, 2 arom. H); 7.61–7.65 (*m*, 1 arom. H); 8.00–8.02 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 25.01 (*q*); 26.14 (*q*); 70.11 (*d*); 71.12 (*t*); 71.61 (*d*); 74.92 (*d*); 98.57 (*d*); 112.41 (*s*); 128.31 (2*d*); 128.35 (*d*); 128.52 (4*d*); 128.73 (*s*); 129.93 (2*d*); 133.78 (*d*); 135.39 (*s*); 164.62 (*s*); 167.03 (*s*). CI-MS (C_4H_9): 400 (19), 399 (100, $[M + 1]^+$), 341 (3), 309 (4), 277 (6), 213 (7), 123 (4), 105 (12), 91 (21). Anal. calc. for $C_{22}H_{22}O_7$ (398.42): C 66.32, H 5.57; found: C 66.09, H 5.59.

Benzyl (5R/S)-5-C-Acetoxy-2-O-benzoyl-3,4-O-isopropylidene-α-L-arabinopyranosides (**28**/**29**), *Benzyl (5S/R)-2-O-Benzoyl-5-C-hydroxy-3,4-O-isopropylidene-α-L-arabinopyranosides* (**30**/**31**) *and (5R)-1-O-Acetyl-2-O-benzoyl-5-C-(benzyloxy)-3,4-O-isopropylidene-α-L-arabinopyranose* (**32**). a) A soln. of crystalline **27** (1.01 g, 2.54 mmol) in THF (11 ml) was treated with 20% DIBAH in hexane (4.81 ml, *ca.* 4.73 mmol) at −80° until TLC (toluene/^{i}PrOH 15:1) showed completion of the reaction (1 h). The soln. was treated with Ac_2O (0.69 ml, 7.35 mmol), stored for 10 days at −20°, treated with a sat. aq. $NaHCO_3$ soln. (10 ml), stirred at r.t. for 30 min, diluted with AcOEt, washed with a sat. aq. $NaHCO_3$ soln. (3 ×), dried, and evaporated. FC (21 g of SiO_2, hexane/AcOEt 5:2) of the residue (1.81 g) and crystallization gave **28**/**29** 1:7 (1.00 g, 89%) as colourless crystals and **30**/**31** 1:7 (0.084 g, 8%) as colourless needles. Anal. samples of **28** and **29** were obtained by repeated chromatography.

b) A soln. of crystalline **30**/**31** 1:7 (0.426 g, 1.06 mmol) in CH_2Cl_2 (3.5 ml) and pyridine (2.0 ml) was treated with Ac_2O (1.5 ml) at −60° for 1 h, slowly warmed to −20°, and stored at −20° for 18 h. Usual workup and FC (11 g of SiO_2, AcOEt/hexane 2:5) gave **28**/**29** 1:7 (0.408 g, 87%) and **32** (0.032 g, 7%) as colourless needles.

Data of **28**: R_f (toluene/^{i}PrOH 15:1) 0.46. $[\alpha]_D^{24.5} = -6.4$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3100*w*, 3070*w*, 3040*w*, 2995*w*, 2960*m*, 2930*m*, 2870*w*, 2860*w*, 1755*s*, 1732*s*, 1605*w*, 1587*w*, 1495*w*, 1455*m*, 1385*s*, 1376*s*, 1320*m*, 1270*s*, 1240*s*, 1200*s*, 1164*s*, 1110*s*, 1096*s*, 1072*s*, 1044*s*, 1030*s*, 1012*s*, 970*s*, 946*s*, 912*s*, 866*m*, 696*m*, 664*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.36, 1.57 (2*s*, 2 Me); 2.18 (*s*, AcO); 4.40–4.45 (*m*, H–C(3), H–C(4)); 4.57 (*d*, $J = 12.5$), 4.80 (*d*, $J = 12.5$, PhCH_2); 4.84 (*d*, $J = 7.5$, H–C(1)); 5.78 (*t*, $J \approx 7.6$, H–C(2)); 6.27 (*d*, $J = 4.0$, H–C(5)); 7.14–7.26 (*m*, 5 arom. H); 7.41–7.55 (*m*, 2 arom. H); 7.58–7.63 (*m*, 1 arom. H); 7.99–8.07 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 21.27 (*q*); 25.28 (*q*); 26.71 (*q*); 69.48 (*t*); 72.60 (*d*); 73.37 (*d*); 75.19 (*d*); 88.86 (*d*); 96.54 (*d*); 110.82 (*s*); 127.69 (2*d*); 127.77 (*d*); 127.90 (2*d*); 128.26 (2*d*); 129.41 (*s*); 128.53 (2*d*); 133.20 (*d*); 136.56 (*s*); 165.01 (*s*); 169.09 (*s*). Anal. calc. for $C_{24}H_{26}O_8$ (442.47): C 65.15, H 5.92; found: C 65.40, H 6.16.

Data of **29**: M.p. 86.3–87.3°. R_f (toluene/^{i}PrOH 15:1) 0.58. $[\alpha]_D^{24.5} = -59.1$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3070*w*, 3040*m*, 2995*m*, 2940*m*, 1760*s*, 1730*s*, 1605*m*, 1588*w*, 1496*w*, 1455*m*, 1386*s*, 1375*s*, 1318*m*, 1304*m*, 1266*s*, 1240*s*, 1200*s*, 1170*m*, 1145*s*, 1110*s*, 1096*s*, 1086*s*, 1072*s*, 1050*s*, 1028*s*, 1002*s*, 950*s*, 930*m*, 912*m*, 858*m*, 698*m*, 664*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.38, 1.59 (2*s*, 2 Me); 2.16 (*s*, AcO); 4.25 (*dd*, $J = 5.6, 5.2$, H–C(4)); 4.43 (*t*, $J = 5.4$, H–C(3)); 4.62 (*d*, $J = 12.2$), 4.94 (*d*, $J = 12.2$ PhCH_2); 4.94 (*d*, $J = 4.7$, H–C(1)); 5.45 (*t*, $J \approx 4.9$, H–C(2)); 6.31 (*d*, $J = 4.9$, H–C(5)); 7.27–7.33 (*m*, 5 arom. H); 7.43–7.47 (*m*, 2 arom. H); 7.58–7.61 (*m*, 1 arom. H); 8.03–8.05 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 20.97 (*q*); 26.06 (*q*); 27.60 (*q*); 69.62 (*t*); 70.82 (*d*); 73.79 (*d*); 75.40 (*d*); 89.46 (*d*); 96.01 (*d*); 110.82 (*s*); 127.86 (*d*); 128.61 (2*d*); 128.36 (4*d*); 129.41 (*s*); 129.88 (2*d*); 133.36 (*d*); 136.56 (*s*); 165.01 (*s*); 169.09 (*s*). CI-MS (C_4H_9): 443 (4, $[M + 1]^+$), 384 (23), 383 (100), 335 (21), 293 (6), 57 (46), 43 (7). Anal. calc. for $C_{24}H_{26}O_8$ (442.47): C 65.15, H 5.92; found: C 65.29, H 5.74.

Data of **30**/**31**: M.p. 116.3–118.9°. R_f (toluene/^{i}PrOH 15:1) 0.20. $[\alpha]_D^{24.5} = -53.5$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3600*w*, 3065*w*, 3030*m*, 3010*m*, 2990*m*, 2900*m*, 1730*s*, 1604*w*, 1586*w*, 1495*w*, 1452*m*, 1385*m*, 1375*m*, 1345*w*, 1315*m*, 1304*m*, 1268*s*, 1245*s*, 1230*m*, 1200*m*, 1178*m*, 1155*m*, 1110*s*, 1095*s*, 1070*s*, 1042*s*, 1026*s*, 1006*s*, 1000*s*, 986*s*, 914*w*, 858*m*, 710*s*, 700*m*, 664*m*. ^{1}H-NMR (400 MHz, $CDCl_3$; **30**/**31** 1:7): signals of **31**: 1.37, 1.59 (2*s*, 2 Me); 3.01 (*d*, $J = 4.8$, exchange with D_2O, HO–C(5)); 4.21 (*dd*, $J = 6.3, 4.6$, H–C(4)); 4.41 (*t*, $J = 6.7$, H–C(3)); 4.67 (*d*, $J = 12,5$), 4.80 (*d*, $J = 12.5$, PhCH_2); 5.01 (*d*, $J = 6.0$, H–C(1)); 5.39 (*t*, $J = 4.5$, addition of $D_2O \rightarrow$ *d*, $J \approx 4.5$, H–C(5)); 5.44 (*dd*, $J = 6.8, 6.2$, H–C(2)); 7.22–7.26 (*m*, 5 arom. H); 7.43–7.47 (*m*, 2 arom. H); 7.57–7.60 (*m*, 1 arom. H); 8.02–8.05 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$; **30**/**31** 1:7): signals of **30**: 25.01 (*q*); 27.01 (*q*); 69.76 (*t*); 72.77 (*d*); 75.88 (*d*); 76.75 (*d*); 90.71 (*d*); 96.37 (*d*); 128.53 (4*d*); 133.80 (*d*); signals of **31**: 25.86 (*q*); 27.50

(*q*); 70.00 (*t*); 72.36 (*d*); 75.51 (*d*); 76.62 (*d*); 91.75 (*d*); 96.07 (*d*); 110.83 (*s*); 127.67 (2*d*); 127.81 (*d*); 128.31 (4*d*); 129.58 (*s*); 129.88 (2*d*); 133.21 (*d*); 137.22 (*s*); 165.21 (*s*). CI-MS (NH_3): 401 (4, $[M + 1]^+$), 399 (5), 384 (6), 383 (24), 294 (15), 293 (100), 235 (5), 147 (4), 91 (8), 57 (14). Anal. calc. for $C_{22}H_{24}O_7$ (400.43): C 65.99, H 6.04; found: C 66.07, H 6.21.

Data of **32**: M.p. 137.2–138.0°. $[\alpha]_D^{24.5} = -19.8$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3070*w*, 3040*w*, 2995*m*, 2940*m*, 1764*s*, 1730*s*, 1605*m*, 1588*w*, 1495*w*, 1455*m*, 1385*s*, 1375*s*, 1318*m*, 1304*m*, 1270*s*, 1245*s*, 1200*s*, 1180*m*, 1165*m*, 1110*s*, 1095*s*, 1080*s*, 1072*s*, 1046*s*, 1030*s*, 1012*s*, 1004*s*, 972*s*, 942*m*, 905*m*, 858*m*, 696*m*, 664*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.36, 1.58 (2*s*, 2 Me); 2.07 (*s*, AcO); 4.28 (*dd*, *J* = 5.7, 2.0, H–C(4)); 4.48 (*dd*, *J* = 7.2, 5.8, H–C(3)); 4.64 (*d*, *J* = 11.4), 5.00 (*d*, *J* = 11.4, PhCH_2); 5.22 (*d*, *J* = 1.9, H–C(5)); 5.46 (*t*, *J* ≈ 7.7, H–C(2)); 6.18 (*d*, *J* = 7.9, H–C(1)); 7.32–7.47 (*m*, 7 arom. H); 7.56–7.59 (*m*, 1 arom. H); 8.03–8.06 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, $CDCl_3$): 20.90 (*q*); 26.14 (*q*); 27.51 (*q*); 70.06 (*t*); 71.50 (*d*); 75.50 (*d*); 75.75 (*d*); 87.74 (*d*); 96.43 (*d*); 110.67 (*s*); 128.20 (*d*); 128.39 (2*d*); 128.52 (4*d*); 129.35 (*s*); 129.86 (2*d*); 133.32 (*d*); 136.40 (*s*); 165.18 (*s*); 169.61 (*s*). CI-MS (NH_3): 384 (24), 383 (100, $[M - AcO]^+$), 371 (5), 369 (5), 335 (5), 313 (6), 263 (13), 180 (7), 57 (54), 43 (15). Anal. calc. for $C_{24}H_{26}O_8$ (442.47): C 65.15, H 5.92; found: C 64.87, H 5.72.

*Benzyl (5*R*)-2-*O*-Benzoyl-3,4-*O*-isopropylidene-5-*C*-(trichloroacetimidoyloxy)-α-*L*-arabinopyranoside* (**33**). A soln. of **30**/**31** 1:7 (0.214 g, 0.534 mmol) and Cl_3CCN (0.67 ml, 6.68 mmol) in $Cl(CH_2)_2Cl$ (3.8 ml) was treated with 7-methyl-1,5,7-triazabicyclo[4.4.0]dec.5.ene (MTBD; 77 µl, 0.536 mmol) at −30°, stirred for 1.5 h, filtered through SiO_2, and evaporated to give crude **33** (0.241 g, *ca.* 83%) which was immediately used for the next step. An anal. sample was purified by FC (hexane/Et_2O 3:1). Oil. R_f (hexane/Et_2O 1:2) 0.67. IR ($CHCl_3$): 3520*w*, 3405*w*, 3350*w*, 3190*w*, 3165*w*, 3130*m*, 2990*m*, 2940*w*, 1730*s*, 1674*s*, 1603*w*, 1586*w*, 1496*w*, 1452*m*, 1413*w*, 1386*m*, 1375*s*, 1330*m*, 1314*s*, 1265*s*, 1244*s*, 1172*s*, 1148*s*, 1108*s*, 1096*s*, 1053*s*, 1028*s*, 1014*s*, 1002*m*, 977*s*, 963*s*, 928*s*, 920*s*, 856*m*, 840*m*, 827*m*, 695*m*, 645*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.40, 1.65 (2*s*, 2 Me); 4.37 (*dd*, *J* = 5.6, 2.6, H–C(4)); 4.48 (*dd*, *J* = 6.4, 5.8, H–C(3)); 4.61 (*d*, *J* = 12.5), 4.92 (*d*, *J* = 12.5, PhCH_2); 5.05 (*d*, *J* = 6.8, H–C(1)); 5.47 (*t*, *J* = 6.7, H–C(2)); 6.60 (*d*, *J* = 2.6, H–C(5)); 7.18–7.23 (*m*, 5 arom. H); 7.44–7.48 (*m*, 2 arom. H); 7.58–7.62 (*m*, 1 arom. H); 8.04–8.07 (*m*, 2 arom. H); 8.78 (*s*, NH). ^{13}C-NMR (50 MHz, $CDCl_3$): 26.28 (*q*); 27.61 (*q*); 70.14 (*t*); 71.59 (*d*); 74.21 (*d*); 75.66 (*d*); 94.42 (*d*); 95.65 (*d*); 110.91 (*s*); 127.77 (*d*); 127.84 (2*d*); 128.31 (4*d*); 129.56 (*s*); 129.95 (2*d*); 133.25 (*d*); 136.66 (*s*); 160.44 (*s*); 165.21 (*s*). CI-MS (NH_3): 546 (1, $[M + 1]^+$), 438 (11), 436 (11), 385 (7), 384 (61), 383 (100), 382 (7), 343 (11), 325 (14), 292 (10), 275 (8), 57 (8).

*Benzyl (5*R*)-2-*O*-Benzoyl-3,4-*O*-isopropylidene-5-*C*-(diphenoxyphosphoryl)-α/β-*L*-arabinopyranosides* (**34**/**35**) *and Benzyl (5*R*)-2-*O*-Benzoyl-3,4-*O*-isopropylidene-5-*C*-phenoxy-α/β-*L*-arabinopyranosides* (**36**/**37**). a) From **28**/**29**: A soln. of **28**/**29** 1:7 (0.83 g, 1.88 mmol) and $(PhO)_3P$ (1.48 ml, 5.63 mmol) in 1,2-dimethoxyethane (12.4 ml) and Et_2O (20 ml) was treated with Me_3SiOTf (0.68 ml, 3.76 mmol) at −110° for 3 h and at 4° for 20 days. Addition of a sat. aq. $NaHCO_3$ soln. (5 ml) and Et_2O (2 ml), stirring for 15 min, dilution with Et_2O (80 ml), washing of the org. phase with sat. aq. $NaHCO_3$ soln., evaporation, and FC (hexane/Et_2O 2:1) gave **34** (510 mg, 44%), **35** (85 mg, 7%), **36** (251 mg, 28%), and **37** (127 mg, 14%).

b) From **33**: A soln. of **33** (241 mg, *ca.* 0.44 mmol) and $P(OPh)_3$ (0.42 ml, 1.60 mmol) in 1,2-dimethoxyethane (3.0 ml) was treated with Me_3SiOTf (0.18 ml, 1.00 mmol) at −17° for 3 h and at 4° for 5 days. Addition of sat. aq. $NaHCO_3$ soln. (5 ml) and Et_2O (2 ml), stirring for 10 min, dilution with Et_2O (30 ml), washing of the org. phase with sat. aq. $NaHCO_3$ soln. (2 × 30 ml), evaporation, and FC (hexane/Et_2O 3:2 → 1:2) gave **34** (96 mg, 35%) and **35** (50 mg, 18%).

Data of **34**: Colourless needles. M.p. 130.0–132.2° (pentane/Et_2O). R_f (hexane/Et_2O 1:2) 0.31. $[\alpha]_D^{24.5} = +68.0$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3070*w*, 3040*w*, 3004*m*, 2940*w*, 1724*s*, 1594*s*, 1490*s*, 1454*m*, 1386*m*, 1378*m*, 1326*w*, 1316*m*, 1292*s*, 1285*s*, 1265*s*, 1245*s*, 1240*s*, 1190*s*, 1164*s*, 1140*s*, 1120*s*, 1095*s*, 1084*s*, 1072*s*, 1040*m*, 1026*s*, 1010*s*, 970*s*, 955*s*, 940*s*, 904*m*, 875*m*, 840*w*, 710*s*, 690*s*, 666*m*, 615*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): see *Tables 1* and *2*; 1.32, 1.47 (2*s*, 2 Me); 4.43 (*d*, *J* = 12.2), 4.62 (*d*, *J* = 12.2, PhCH_2); 7.15–7.37 (*m*, 15 arom. H); 7.44–7.44 (*m*, 2 arom. H); 7.58–7.61 (*m*, 1 arom. H); 8.05–8.07 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): see *Table 3*; 26.24 (*q*); 27.76 (*q*); 70.01 (*t*); 110.63 (*s*); 120.59 (*d*); 120.64 (*d*); 120.80 (*d*); 120.84 (*d*); 125.05 (*d*); 125.41 (*d*); 127.56 (2*d*); 128.01 (*d*); 128.35 (2*d*); 128.42 (2*d*); 129.38 (2*d*); 129.49 (*s*); 129.85 (2*d*); 129.90 (2*d*); 133.29 (*d*); 136.36 (*s*); 150.25 (*d*, *J*(P,C) = 8.8); 150.68 (*d*, *J*(P,C) = 8.8); 165.83 (*s*). CI-MS (NH_3): 618 (37), 617 (97, $[M + 1]$), 510 (8), 509 (28), 455 (7), 57 (100), 43 (14). Anal. calc. for $C_{34}H_{33}O_9P$ (616.61): C 66.23, H 5.39, P 5.02; found: C 67.68, H 5.74, P 4.84.

Data of **35**: Colourless needles. M.p. 125.6–127.1° (pentane/Et_2O). R_f (hexane/Et_2O 1:2) 0.17. $[\alpha]_D^{25} = -31.0$ (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): 3070*w*, 3030*w*, 3010*m*, 2940*w*, 1730*s*, 1592*m*, 1490*s*, 1452*m*, 1386*m*, 1375*m*, 1316*m*, 1300*m*, 1270*s*, 1245*s*, 1190*s*, 1160*s*, 1138*s*, 1108*s*, 1096*m*, 1070*s*, 1050*m*, 1028*s*, 1010*m*, 960*s*, 940*s*, 904*w*, 875*m*, 840*w*, 710*s*, 690*m*, 670*s*, 646*w*, 616*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): see *Tables 1* and *2*; 1.31, 1.54 (2*s*, 2 Me); 4.58 (*d*, *J* = 12.7), 4.85 (*d*, *J* = 12.7, PhCH_2); 7.17–7.39 (*m*, 15 arom. H); 7.44–7.47 (*m*, 2 arom. H); 7.57–7.60 (*m*, 1 arom. H); 7.99–8.01 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): see *Table 3*; 26.11 (*q*); 27.36 (*q*); 111.45 (*s*); 120.67

(*d*); 120.73 (*d*); 120.84 (*d*); 120.89 (*d*); 125.10 (*d*); 125.52 (*d*); 127.83 (*d*); 127.86 (*d*); 128.33 (3*d*); 129.37 (3*d*); 129.67 (*s*); 129.88 (4*d*); 133.20 (2*d*); 136.54 (*s*); 150.21 (*d*, *J*(P,C) = 7.1); 150.70 (*d*, *J*(P,C) = 7.4); 165.17 (*s*). CI-MS (NH_3): 618 (4), 617 (12, $[M + 1]^+$), 565 (5), 527 (4), 511 (6), 510 (27), 509 (100), 494 (3), 493 (13), 289 (3), 93 (10), 57 (74), 43 (10). Anal. calc. for $C_{34}H_{33}O_9P$ (616.61): C 66.23, H 5.39, P 5.02; found: C 66.49, H 5.65, P 4.81.

Data of **36**: Oil. R_f (hexane/Et_2O 1:2) 0.66. IR ($CHCl_3$): 3040*w*, 3010*w*, 2990*w*, 2940*w*, 1730*s*, 1598*s*, 1498*s*, 1470*m*, 1452*m*, 1386*m*, 1375*m*, 1344*m*, 1315*m*, 1270*s*, 1180*m*, 1166*m*, 1152*m*, 1112*s*, 1096*s*, 1072*s*, 1058*s*, 1028*s*, 1000*m*, 985*s*, 886*w*, 865*w*, 830*w*, 812*w*, 710*s*, 692*m*, 665*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.41, 1.66 (2*s*, 2 Me); 4.37 (*d*, *J* = 12.6), 4.69 (*d*, *J* = 12.6, PhCH_2); 4.51 (*dd*, *J* = 7.4, 6.0, H–C(3)); 4.88 (*d*, *J* = 7.6, H–C(1)); 5.47 (*t*, *J* = 7.6, H–C(2)); 5.96 (*d*, *J* = 2.4, H–C(5)); 6.88–7.47 (*m*, 12 arom. H); 7.57–7.60 (*m*, 1 arom. H); 8.00–8.04 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 26.13 (*q*); 27.56 (*q*); 69.88 (*t*); 72.69 (*d*); 75.75 (*d*); 75.90 (*d*); 94.10 (*d*); 94.80 (*d*); 110.90 (*s*); 116.13 (2*d*); 122.60 (*d*); 127.66–129.90 (several *d*); 133.1 (*d*); 136.50 (*s*); 155.67 (*s*); 165.24 (*s*). CI-MS (NH_3): 478 (5, $[M + 1]^+$), 384 (23), 383 (100), 370 (20), 369 (86), 327 (17), 57 (15).

Data of **37**: Oil. R_f (hexane/Et_2O 1:2) 0.66. IR ($CHCl_3$): 3070*w*, 3050*w*, 3010*m*, 2995*w*, 2940*w*, 1760*w*, 1724*s*, 1600*w*, 1590*w*, 1495*m*, 1454*w*, 1386*w*, 1375*w*, 1330*w*, 1318*w*, 1290*m*, 1266*s*, 1258*m*, 1242*m*, 1235*s*, 1226*w*, 1215*w*, 1205*w*, 1198*m*, 1180*m*, 1172*m*, 1162*w*, 1135*w*, 1116*s*, 1096*m*, 1072*s*, 1040*s*, 1030*s*, 1010*m*, 1000*m*, 985*m*, 958*w*, 928*w*, 905*w*, 892*w*, 875*w*, 865*w*, 855*w*, 835*w*, 922*w*, 815*w*, 795*m*, 735*m*, 712*s*, 695*m*, 680*w*, 665*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.43, 1.57 (2*s*, 2 Me); 4.37 (*d*, *J* = 12.3), 4.69 (*d*, *J* = 12.3, PhCH_2); 4.72 (*dd*, *J* = 6.8, 3.4, H–C(4)); 4.87 (*t*, *J* = 6.9, H–C(3)); 5.21 (*d*, *J* = 2.9, H–C(1)); 5.30 (*dd*, *J* = 7.2, 2.9, H–C(2)); 5.72 (*d*, *J* = 3.2, H–C(5)); 7.04–7.41 (*m*, 10 arom. H); 7.45–7.48 (*m*, 2 arom. H); 7.58–7.61 (*m*, 1 arom. H); 8.10–8.12 (*m*, 2 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 25.47 (*q*); 27.44 (*q*); 69.80 (*t*); 72.03 (*d*); 72.66 (*d*); 76.21 (*d*); 95.31 (*d*); 96.78 (*d*); 109.62 (*s*); 115.87 (2*d*); 122.07 (*d*); 125.67 (*s*); 127.51 (2*d*); 127.56 (*d*); 128.11 (2*d*); 128.25 (2*d*); 129.28 (*s*); 129.47 (2*d*); 129.83 (2*d*); 133.20 (*d*); 136.94 (*s*); 156.83 (*s*); 165.70 (*s*). CI-MS (NH_3): 478 (5, $[M + 1]^+$), 419 (6), 392 (5), 385 (4), 384 (25), 383 (100), 370 (4), 369 (20), 332 (6), 327 (11), 279 (7), 57 (67), 43 (9).

*(5*R*)- and (5*S*)-3-*O*-Acetyl-5-*C*-(diphenoxyphosphoryl)-1,2-*O*-isopropylidene-α-*D*-xylofuranose* (**40** and **41**, resp.). A soln. of **38** [44] (2.00 g, 7.63 mmol) in H_2O (30 ml) was treated with $NaIO_4$ (1.80 g, 8.42 mmol), stirred for 15 min, treated again with $NaIO_4$ (0.70 g, 3.27 mmol), stirred for 1 h, and extracted with $CHCl_3$ (10 × 15 ml) [43]. Evaporation of the combined org. phases gave crude **39** (1.75 g, purity *ca.* 65% (^{1}H-NMR)). The residue was dissolved in CH_2Cl_2 (12 ml), treated with freshly distilled $HP(O)(OPh)_2$ (1.75 ml, 9.09 mmol) and $^iPr_2EtN$ (0.1 ml, 0.58 ml), stirred for 30 min, and evaporated. FC (150 g of SiO_2, hexane/AcOEt 2:1) gave **40**/**41** 5:1 (^{1}H-NMR; 1.75 g, 49% from **38**).

Data of **40**: Colourless crystals. M.p. 136.5–137.5° (hexane/CH_2Cl_2). R_f (hexane/AcOEt 1:1) 0.17. $[\alpha]_D^{25} = -35.3$ (*c* = 1.18, $CHCl_3$). IR ($CHCl_3$): 3558*w*, 3298*w*, 3008*m*, 2940*w*, 1747*s*, 1592*m*, 1490*s*, 1456*w*, 1385*m*, 1376*s*, 1163*s*, 1090*s*, 1072*s*, 1026*s*, 1009*m*, 950*s*, 904*m*, 854*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Tables 1* and *2*; 1.33, 1.50 (2*s*, 2 Me); 2.05 (*s*, AcO); 3.99 (br. *s*, exchange with CD_3OD, OH); 7.14–7.34 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; 20.70 (*q*); 26.39 (*q*); 26.75 (*q*); 112.57 (*s*); 120.74 (*d*); 120.80 (*d*); 120.87 (*d*); 120.95 (*d*); 125.34 (2*d*); 129.66 (2*d*); 129.72 (2*d*); 150.16 (*d*, *J*(P,C) = 10.0); 150.28 (*d*, *J*(P,C) = 9.8); 169.95 (*s*). FAB-MS (3-NOBA): 466 (26), 465 (100, $[M + 1]^+$), 347 (41), 329 (31), 235 (21). Anal. calc. for $C_{22}H_{25}O_9P$ (464.41): C 56.90, H 5.43, P 6.67; found: C 56.83, H 5.55, P 6.93.

Data of **41**: Solid. R_f (hexane/AcOEt 1:1) 0.17. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Tables 1* and *2*; 1.33, 1.49 (2*s*, 2 Me); 2.02 (*s*, AcO); 2.33 (br. *s*, OH); 7.15–7.22 (*m*, 6 arom. H); 7.29–7.35 (*m*, 4 arom. H).

*(5*R*)-3,5-Di-*O*-acetyl-5-*C*-(diphenoxyphosphoryl)-1,2-*O*-isopropylidene-α-*D*-xylofuranose* (**42**). A soln. of **40**/**41** 5:1 (300 mg, 0.65 mmol) in CH_2Cl_2 (6 ml) was treated with Ac_2O (200 µl) and pyridine (30 µl) and stirred at *ca.* 23° for 6 h. Evaporation, FC (30 g of SiO_2, hexane/AcOEt 3:1) of the resulting oil (282 mg, 86%), and crystallization gave **42** (130 mg, 40%). Colourless crystals. M.p. 111.0–112.5° (hexane/AcOEt). R_f (hexane/AcOEt 1:1) 0.39. $[\alpha]_D^{25} = -18.3$ (*c* = 0.92, $CHCl_3$). IR ($CHCl_3$): 3008*m*, 2940*w*, 1752*s*, 1592*m*, 1491*s*, 1456*w*, 1430*w*, 1375*s*, 1276*m*, 1163*s*, 1095*m*, 1070*s*, 1054*m*, 1026*s*, 1009*m*, 952*s*, 904*m*, 888*w*, 854*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Tables 1* and *2*; 1.32, 1.51 (2*s*, 2 Me); 1.98, 2.06 (2*s*, 2 AcO); 7.15–7.33 (*m*, 10 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 3*; 20.37 (*q*); 20.74 (*q*); 26.39 (*q*); 26.83 (*q*); 112.83 (*s*); 120.35 (*d*); 120.38 (*d*); 120.64 (*d*); 120.68 (*d*); 125.29 (*d*); 125.36 (*d*); 129.71 (2*d*); 129.76 (2*d*); 150.13 (*d*, *J*(P,C) = 9.4); 150.49 (*d*, *J*(P,C) = 9.1); 168.69 (*d*, *J*(P,C) = 3.1); 169.62 (*s*). FAB-MS (3-NOBA): 508 (39), 507 (100, $[M + 1]^+$), 449 (27), 389 (51), 347 (42), 329 (71). Anal. calc. for $C_{24}H_{27}O_{10}P$ (506.44): C 56.92, H 5.37; found: C 56.76, H 5.14.

*(5*R*)-1,2,3,4-Tetra-*O*-acetyl-5-*C*-(diphenoxyphosphoryl)-α/β-*D*-xylopyranoses* (**43**/**44**). a) From **40**: A soln. of crystalline **40** (100 mg, 0.215 mmol) in AcOEt/HCO_2H/H_2O 4:4:1 (2.25 ml) was stirred at 50° for 12 h and evaporated. The residue was suspended in a mixture of AcOEt (5 ml) and Ac_2O (1.2 ml), treated dropwise with pyridine (1.2 ml), and stirred for 2 h. Evaporation and FC (20 g of SiO_2, hexane/AcOEt 2:1) gave **43**/**44** 3:2 (^{1}H-NMR; 80 mg, 67%). Pure samples of **43** and **44** were obtained by HPLC (hexane/AcOEt 1:1).

b) From crude **40**/**41**: A soln. of crude **40**/**41** 3:1 (1.92 g, *ca.* 4.13 mmol) in CF_3CO_2H (27 ml) was cooled to 0°, treated dropwise with H_2O (3 ml), stirred for 2 h, and evaporated (14 h, 0.2 mbar, no heating). The residue (1.76 g) was suspended in pyridine/Ac_2O 2:1 (30 ml) and stirred for 2 h. Evaporation and FC (100 g of SiO_2, hexane/AcOEt 1:1) gave **43**/**44** 3:2 (1.10 g, 48%).

c) Large-scale, one-pot procedure starting from **38**: A soln. of **38** (60.0 g, 229 mmol) in H_2O (900 ml) was treated with $NaIO_4$ (55.0 g, 257 mmol), stirred for 15 min, and treated again with $NaIO_4$ (17.0 g, 79 mmol). After 1 h, the soln. was extracted with $CHCl_3$ (10 × 300 ml) and the combined org. phase evaporated. The residue was dissolved in CH_2Cl_2 (300 ml), treated with freshly distilled $HP(O)(OPh)_2$ (53 ml, 275 mmol) and $^iPr_2EtN$ (2 ml, 12 mmol), stirred for 30 min, and evaporated. The residue (110 g) was dissolved in AcOEt/HCO_2H/H_2O 4:4:1 (536 ml), heated to reflux for 90 min, and evaporated. The residue was suspended in toluene (800 ml) and 1,4-dioxane (300 ml). H_2O and HCO_2H were removed in a *Dean-Stark* apparatus at *ca.* 80 mbar. After evaporation, the residue was suspended in Ac_2O (120 ml) and treated with 70% $HClO_4$ soln. (4 × 2 ml) under vigorous shaking until a clear reddish soln. was formed. The soln. was poured on ice (*ca.* 600 ml), treated with pyridine (10 ml) and $CHCl_3$ (250 ml), and vigorously stirred for 60 min. Phase-separation, extraction of the aq. phase with $CHCl_3$ (3 × 250 ml), washing of the combined org. phases with sat. aq. $NaHCO_3$ soln. (→ pH 11), drying ($MgSO_4$), evaporation, and FC (800 g of SiO_2, hexane/AcOEt 1:1) gave **43**/**44** 3:2 (^{1}H-NMR; 19.8 g, 16%).

Data of **43**: Colourless oil. R_f (hexane/AcOEt 1:1) 0.21. $[\alpha]_D^{25} = +98.2$ ($c = 0.62$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 2959*w*, 1758*s*, 1591*m*, 1490*s*, 1371*m*, 1161*s*, 1084*m*, 1047*s*, 1026*m*, 1010*m*, 986*w*, 957*s*, 986*w*, 957*s*, 906*w*, 838*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Tables 1* and *2*; 2.03, 2.04, 2.05, 2.12 (4*s*, 4 AcO); 7.17–7.37 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; 20.44 (*q*); 20.66 (2*q*); 20.75 (*q*); 120.66 (*d*); 120.78 (*d*); 125.73 (2*d*); 129.85 (2*d*); 129.89 (2*d*); 149.59 (*d*, J(P,C) = 9.6); 149.66 (*d*, J(P,C) = 8.0); 168.41 (*s*); 169.28 (*s*); 169.56 (*s*); 170.09 (*s*). FAB-MS (3-NOBA): 552 (10), 551 (33, $[M + 1]^+$), 457 (21), 330 (31), 329 (100), 301 (12). Anal. calc. for $C_{25}H_{27}O_{12}P$ (550.45): C 54.55, H 4.94; found: C 54.55, H 4.81.

Data of **44**: Colourless crystals. M.p. 107.0–108.0° (hexane/Et_2O). R_f (hexane/AcOEt 1:1) 0.24. $[\alpha]_D^{25} = +32.4$ ($c = 0.50$, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 1762*s*, 1591*m*, 1490*s*, 1369*m*, 1273*m*, 1161*m*, 1073*s*, 1040*s*, 958*s*, 906*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Tables 1* and *2*; 2.01, 2.04, 2.06, 2.14 (4*s*, 4 AcO); 7.14–7.22 (*m*, 6 arom. H); 7.30–7.38 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; 20.57 (2*q*); 20.64 (*q*); 20.78 (*q*); 120.73 (*d*); 120.79 (*d*); 120.83 (*d*); 120.88 (*d*); 125.66 (*d*); 125.82 (*d*); 129.77 (2*d*); 129.98 (2*d*); 149.60 (*d*, J(P,C) ≈ 8.6); 149.73 (*d*, J(P,C) ≈ 11.1); 168.87 (*s*); 169.14 (*s*); 169.28 (*s*); 169.99 (*s*). FAB-MS (3-NOBA): 551 (5, $[M + 1]^+$), 492 (11), 491 (40), 457 (6), 389 (12), 330 (26), 329 (100), 308 (8), 307 (30), 289 (17), 253 (14). Anal. calc. for $C_{25}H_{27}O_{12}P$ (550.45): C 54.55, H 4.94; found: C 54.35, H 4.83.

*(5*R*)-1,2,3,4-Tetra-*O*-acetyl-5-C-[bis(benzyloxy)phosphoryl]-α/β-*D*-xylopyranoses* (**45**/**46**) *and (5*R*)-1,2,3,4-Tetra-*O*-acetyl-5-C-[(benzyloxy)phenoxyphosphoryl]-β-*D*-xylopyranose* (**47**). a) From **43**/**44** by transesterification: A soln. of **43**/**44** 3:2 (2.02 g, 3.66 mmol) in THF (20 ml) was treated with BnOH (7.5 ml), KF (2.1 g, 36.1 mmol), and [18]crown-6 (0.31 g, 1.14 mmol) at *ca.* 23° and stirred for 5 h. Filtration through SiO_2 (30 g), elution with hexane/AcOEt 1:3, evaporation, and FC (200 g of SiO_2, hexane/AcOEt 3:1 → 1:1 → 1:2) gave **45**/**46** 3:2 (1.24 g, 58%), **47** (0.05 g, 2%), and **48**/**49** (0.18 g, 9%). The mixture **45**/**46** was separated by HPLC (hexane/AcOEt 1:1).

b) From **43**/**44** by transesterification and acetylation: A soln. of **43**/**44** 3:2 (19.8 g, 35.97 mmol) in THF (300 ml) was treated with BnOH (74 ml), KF (20.9 g, 360 mmol), and [18]crown-6 (2.85 g, 10.78 mmol) at *ca.* 23°, stirred for 5 h, filtered through SiO_2 (elution with hexane/AcOEt 1:3), and evaporated. The residue was dissolved in pyridine (300 ml) and Ac_2O (150 ml) and stirred for 12 h. Usual workup ($CHCl_3$, washing with H_2O, H_2SO_4, and $NaHCO_3$ soln.) and FC (800 g of SiO_2, hexane/AcOEt 1:1) gave **45**/**46** 3:2 (9.2 g, 44%).

Data of **45**/**46**: FAB-MS (3-NOBA): 580 (5), 579 (15, $[M + 1]^+$), 520 (4), 519 (15), 417 (18), 357 (30), 309 (19), 267 (32), 207 (10), 181 (17), 92 (26), 91 (100).

Data of **45**: Colourless oil. R_f (hexane/AcOEt 1:1) 0.16. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Tables 1* and *2*; 1.78, 2.00, 2.01, 2.13 (4*s*, 4 AcO); 5.04 (*dd*, J = 11.6, 7.4), 5.09 (*dd*, J = 11.6, 8.6, PhCH_2); 5.04 (*d*, J = 9.1, PhCH_2); 7.27–7.40 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; 20.36 (*q*); 20.41 (*q*); 20.63 (*q*); 20.81 (*q*); 68.72 (*dt*, J(P,C) = 7.1); 69.02 (*dt*, J(P,C) = 6.8); 128.10–129.80 (several *d*); 135.60 (*d*, J(P,C) ≈ 5.0); 135.67 (*d*, J(P,C) ≈ 4.8); 168.42 (*s*); 169.20 (*s*); 169.56 (*s*); 170.11 (*s*).

Data of **46**: Colourless crystals. M.p. 135.5–137.0° (hexane/CH_2Cl_2). R_f (hexane/AcOEt 1:1) 0.16. $[\alpha]_D^{25} = +11.9$ ($c = 1.23$, $CHCl_3$). IR ($CHCl_3$): 3008*m*, 2963*w*, 1762*s*, 1498*w*, 1456*w*, 1430*w*, 1369*m*, 1073*s*, 1040*s*, 998*s*, 920*w*, 891*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Tables 1* and *2*; 1.81, 2.01, 2.03, 2.10 (4*s*, 4 AcO); 5.03 (*d*, J = 8.6, PhCH_2); 5.07 (*d*, J = 8.0, PhCH_2); 7.30–7.40 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; 20.40 (*q*); 20.53 (2*q*); 20.74 (*q*); 68.58 (*dt*, J(P,C) = 6.8); 69.08 (*dt*, J(P,C) = 6.6); 128.11–128.63 (several *d*); 135.56 (*d*, J(P,C) = 5.8); 135.69 (*d*, J(P,C) = 6.1); 168.71 (*s*); 169.13 (*s*); 169.22 (*s*); 169.97 (*s*). Anal. calc. for $C_{27}H_{31}O_{12}P$ (578.51): C 56.06, H 5.40, P 5.35; found: C 55.94, H 5.27, P 5.57.

Data of **47**: Colourless crystals. M.p. 131.0–132.0° (hexane/Et_2O). R_f (hexane/AcOEt 1:1) 0.21. IR ($CHCl_3$): 3008*w*, 1761*s*, 1592*w*, 1490*m*, 1456*w*, 1430*w*, 1370*m*, 1163*m*, 1073*s*, 1040*s*, 1000*m*, 944*m*, 904*w*, 863*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Tables 1* and *2*; 1.95, 2.02, 2.03, 2.11 (4*s*, 4 AcO); 5.20 (*d*, J = 8.1, PhCH_2); 7.13–7.37 (*m*, 10 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): see *Table 3*; 20.53 (2*q*); 20.58 (*q*); 20.75 (*q*); 69.84 (*dt*, J(P,C) = 6.6); 120.88 (*d*); 120.92 (*d*); 125.56 (*d*); 128.34 (2*d*); 128.59 (2*d*); 128.70 (*d*); 129.85 (2*d*); 135.41 (*d*, J(P,C) = 6.2); 149.63 (*d*, J(P,C) = 8.2); 168.80 (*s*); 169.14 (*s*); 169.40 (*s*); 169.94 (*s*). FAB-MS (3-NOBA): 655 (4, $[M + 91]^+$), 506 (9), 505 (35), 403 (31), 344 (24), 343 (100), 295 (28), 267 (10), 254 (10), 253 (82), 225 (11). Anal. calc. for $C_{26}H_{29}O_{12}P$ (564.48): C 55.32, H 5.18; found: C 55.60, H 5.21.

*(5*R*)-2,3,4-Tri-*O*-acetyl-5-*C*-[bis(benzyloxy)phosphoryl]-α/β-*D*-xylopyranoses* (**48**/**49**). a) From **45**/**46**: A soln. of **45**/**46** 3:2 (8.10 g, 14.0 mmol) in DMF (150 ml) was treated with $(NH_4)_2CO_3$ (4.05 g) at *ca.* 23°, stirred for 4 h 20 min, cooled to 0°, diluted with CH_2Cl_2 (300 ml) and H_2O (900 ml), and shaken vigorously. The combined org. layers were separated and washed with 1M H_2SO_4 and sat. aq. $NaHCO_3$ soln. Drying ($MgSO_4$), evaporation, and FC (240 g of SiO_2, hexane/AcOEt 1:2) gave **48**/**49** 7:1 (6.50 g, 86%).

b) From **43**/**44**: A soln. of **43**/**44** 3:2 (1.00 g, 3.30 mmol) in BnOH (3.7 ml) was treated with $Ti(O^iPr)_4$ (0.8 ml) at 60° and stirred for *ca.* 90 min. Workup [45] and FC (hexane/AcOEt 3:2 → 1:1 → 1:3) gave **48**/**49** 7:1 (341 mg, 35%). Long colourless needles. M.p. 100.5–102.0° (CH_2Cl_2/hexane). R_f (hexane/AcOEt 1:3) 0.25. $[\alpha]_D^{25}$ = +90.2 (*ca.* 10 min) → 73.2 (24 h) (c = 1.30, $CHCl_3$). IR ($CHCl_3$): 3550*w*, 3275*w*, 3069*w*, 3008*m*, 2962*w*, 1752*s*, 1603*w*, 1456*m*, 1369*m*, 1161*m*, 1040*s*, 1009*s*, 999*s*, 965*m*, 922*w*, 887*w*, 601*m*. ^{1}H-NMR (500 MHz, $CDCl_3$; **48**/**49** 7:1): signals of **48**: see *Tables 1* and *2*; 1.66, 1.98, 2.02 (3*s*, 3 AcO); 4.95 (*dd*, J = 11.5, 7.0), 5.04 (*dd*, J = 11.5, 8.2, PhCH_2); 5.08 (*d*, J = 9.3, PhCH_2); 7.28–7.58 (*m*, 10 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$; **48**/**49** 7:1): signals of **48**: see *Table 3*; 20.29 (*q*); 20.68 (*q*); 20.71 (*q*); 68.42 (*dt*, J(P,C) = 6.7); 69.10 (*dt*, J(P,C) = 6.6); 128.17–128.77 (several *d*); 135.42 (*d*, J(P,C) = 6.8); 135.87 (*d*, J(P,C) = 5.1); 169.34 (*s*); 170.02 (*s*); 170.17 (*s*). ^{31}P-NMR (121 MHz, $CDCl_3$; **48**/**49** 7:1): signals of **49**: 17.45. FAB-MS (3-NOBA): 538 (31), 537 (100, $[M + 1]^+$), 391 (22), 307 (26), 155 (18), 154 (44), 138 (23), 137 (41), 136 (33), 123 (17), 91 (54). Anal. calc. for $C_{25}H_{29}O_{11}P$ (536.47): C 55.97, H 5.45, P 5.77; found: C 55.96, H 5.63, P 5.49.

*(5*R*)-2,3,4-Tri-*O*-acetyl-5-*C*-[bis(benzyloxy)phosphoryl]-α/β-*D*-xylopyranosyl Trichloroacetimidates* (**50**/**51**). A vigorously stirred soln. of **48**/**49** (1.00 g, 1.86 mmol) in CH_2Cl_2 (10 ml) and Cl_3CCN (1.90 ml, 18.5 mmol) was treated with K_2CO_3 (2.0 g) at 21° and stirred for 75 min. FC (20 g of SiO_2, hexane/AcOEt 1:2) gave **50**/**51** 7:1 (1.11 g, 87%). Colourless oil. R_f (hexane/AcOEt 1:2) 0.39 (**50**), 0.32 (**51**). IR ($CHCl_3$): 3346*w*, 3008*w*, 2960*w*, 1755*s*, 1677*m*, 1498*w*, 1456*w*, 1428*w*, 1369*m*, 1290*m*, 1137*w*, 1043*s*, 999*s*, 972*s*, 937*w*, 912*w*, 888*w*, 833*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; **50**/**51** 7:1): see *Tables 1* and *2*; 1.82, 2.00, 2.01 (3*s*, 3 AcO); 5.01 (*d*, J = 8.1, PhCH_2); 5.05 (*dd*, J = 11.7, 7.4), 5.10 (*dd*, J = 11.6, 8.8, PhCH_2); 7.28–7.38 (*m*, 10 arom. H); 8.68 (br. *s*, NH). ^{13}C-NMR (75 MHz, $CDCl_3$; **50**): see *Table 3*; 20.44 (2*q*); 20.67 (*q*); 68.51 (*dt*, J(P,C) = 6.6); 69.08 (*dt*, J(P,C) = 6.7); 90.50 (*s*); 127.98–128.59 (several *d*); 135.63 (*d*, J(P,C) ≈ 6.1); 135.71 (*d*, J(P,C) ≈ 6.1); 160.52 (*s*); 169.36 (*s*); 169.77 (*s*); 169.87 (*s*). ^{31}P-NMR (121 MHz, $CDCl_3$; **50**/**51** 7:1): 17.03 (**50**); 15.42 (**51**). FAB-MS (3-NOBA): 772 (3), 772 (4), 770 (3), 770 (3, $[M + 91]^+$), 769 (4), 704 (4), 702 (4, $[M + Na]^+$), 627 (12), 537 (15), 519 (24), 418 (12), 417 (47), 358 (25), 357 (99), 309 (50), 279 (12), 268 (18), 267 (100), 237 (11), 219 (19), 197 (19), 182 (14), 181 (73).

*4-Methyl-2-oxo-2*H*-1-benzopyran-7-yl (5*R*)-2,3,4-Tri-*O*-acetyl-5-*C*-[bis(benzyloxy)phosphoryl]-β-*D*-xylopyranoside* (**52**). A mixture of **50**/**51** 7:1 (407 mg, 0.60 mmol), 4-methyl-7-(trimethylsilyloxy)-2*H*-1-benzopyran-2-one (220 mg, 0.89 mmol), and powdered 3-Å molecular sieves (*ca.* 1 g) in CH_2Cl_2 (4 ml) was treated with a soln. of $BF_3 \cdot OEt_2$ (60 µl, 0.48 mmol) in CH_2Cl_2 (1.0 ml) at −20°, allowed to warm to 23° within 2 h, cooled to −20°, treated with pyridine (0.6 ml) and Ac_2O (0.3 ml), allowed to warm to 23°, and stirred for 2 h. After the addition of ice and $CHCl_3$, the mixture was shaken and the aq. phase extracted with $CHCl_3$. The combined org. phases were washed with 0.5M H_2SO_4 and a sat. soln. of $NaHCO_3$, dried ($MgSO_4$), and evaporated. FC (30 g of SiO_2, hexane/AcOEt 1:1) gave **52** (190 mg, 30%). M.p. 148.5–149.5° (Et_2O/hexane). R_f (hexane/AcOEt 1:3) 0.32. $[\alpha]_D^{25}$ = −45.6 (c = 0.57, $CHCl_3$). IR ($CHCl_3$): 3008*m*, 2900*w*, 1756*s*, 1615*m*, 1498*w*, 1456*w*, 1428*w*, 1370*m*, 1327*w*, 1160*m*, 1137*m*, 1068*s*, 1042*s*, 1015*s*, 999*s*, 965*m*, 885*m*, 857*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Tables 1* and *2*; 1.86, 2.03, 2.05 (3*s*, 3 AcO); 2.37 (*d*, J = 1.2, Me); 4.96 (*dd*, J = 11.6, 8.0, PhCH); 5.00–5.07 (*m*, 3 PhCH); 6.19 (br. *d*, J = 1.2, H–C(3′)); 6.89 (*dd*, J = 9.4, 2.5, H–C(6′)); 6.89 (*d*, J = 2.3, H–C(8′)); 7.27–7.33 (*m*, 10 arom. H); 7.36 (*d*, J = 9.4, H–C(5′)). ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 3*; 18.66 (*q*); 20.45 (*q*); 20.58 (2*q*); 68.49 (*dt*, J(P,C) = 6.7); 69.33 (*dt*, J(P,C) = 6.6); 104.64 (*d*); 113.41 (*d*); 113.44 (*d*); 115.76 (*s*); 125.83 (*d*); 128.22–128.68 (several *d*); 135.51 (*d*, J(P,C) = 6.0); 135.58 (*d*, J(P,C) = 5.9); 151.93 (*s*); 154.74 (*s*); 159.03 (*s*); 160.61 (*s*); 169.15 (*s*); 169.27 (*s*); 170.10 (*s*). FAB-MS (3-NOBA): 696 (20), 695 (61, $[M + 1]^+$), 622 (36), 532 (40), 519 (25), 460 (38), 417 (30), 400 (31), 399 (100), 391 (32), 371 (42), 357 (68). Anal. calc. for $C_{35}H_{35}O_{13}P$ (694.62): C 60.52, H 5.08, P 4.46; found: C 60.26, H 5.21, P 4.25.

*4-Methyl-2-oxo-2*H*-1-benzopyran-7-yl (5*R*)-5-*C*-[Bis(benzyloxy)phosphoryl]-β-*D*-xylopyranoside* (**53**). A

suspension of **52** (107.8 mg, 0.155 mmol) in MeOH (4 ml) was treated with a sat. soln. of NH_3 in MeOH (4 ml) at 0°, allowed to warm to *ca.* 23° when it became clear, and stirred for 1.5 h. Evaporation gave **53** (92 mg, 99%). R_f (AcOEt/MeOH/H_2O 7:2:1) 0.42. ^{1}H-NMR (300 MHz, CD_3OD): see *Tables 1* and *2*; 2.37 (*d*, *J* = 1.2, Me); 4.93 (*dd*, *J* = 11.8, 7.4), 5.00 (*dd*, *J* = 11.7, 6.7, PhCH_2); 5.11 (*d*, *J* = 6.7, PhCH_2); 6.15 (br. *d*, *J* = 1.2, H–C(3′)); 7.00 (*d*, *J* = 2.3, H–C(8′)); 7.03 (*dd*, *J* = 8.7, 2.5, H–C(6′)); 7.12–7.42 (*m*, 10 arom. H); 7.50 (*d*, *J* = 8.7, H–C(5′)). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 3*; 18.71 (*q*); 69.66 (*dt*, *J*(P,C) = 6.3); 69.86 (*dt*, *J*(P,C) = 6.9); 104.89 (*d*); 113.14 (*d*); 115.07 (*d*); 116.28 (*s*); 127.34 (*d*); 128.75–129.59 (several *d*); 137.38 (*d*, *J*(P,C) = 6.5); 137.59 (*d*, *J*(C,P) = 6.2); 155.31 (*s*); 155.95 (*s*); 161.37 (*s*); 163.16 (*s*).

*4-Methyl-2-oxo-2*H*-1-benzopyran-7-yl (5*R*)-5-*C*-Phosphono-β-*D*-xylopyranoside Disodium Salt* (**4**). A deoxygenated soln. of **53** (92 mg, *ca.* 0.155 mmol) in MeOH (4 ml) and HCO_2H (150 µl) was treated with 10% Pd/C (80 mg) at *ca.* 23°, stirred for 2 h, and filtered through *Hyflo Super Cel*® and silylated SiO_2 (*Merck*, 0.063–0.200 mm). The filtrate was evaporated, the residue dissolved in MeOH, and the soln. poured on a column packed with *Dowex*® *50W X2* 50–100 mesh (Na^+ form). Elution with H_2O and lyophilization gave **4** (61 mg, 91%). IR (KBr): 3650–3000*s*, 2919*m*, 1718*s*, 1615*s*, 1560*w*, 1508*w*, 1425*w*, 1391*m*, 1369*w*, 1276*s*, 1164*s*, 1055*s*, 1019*s*, 968*w*, 918*w*, 853*w*, 807*w*. ^{1}H-NMR (300 MHz, D_2O): see *Tables 1* and *2*; 2.21 (br. *s*, Me); 3.58–3.72 (*m*, 4 H); 5.96 (br. *s*, H–C(3′)); 6.80 (*d*, *J* = 2.3, H–C(8′)); 6.98 (*dd*, *J* = 8.9, 2.3, H–C(6′)); 7.45 (*d*, *J* = 8.8, H–C(5′)). ^{13}C-NMR (75 MHz, D_2O): see *Table 3*; 20.62 (*q*); 106.42 (*d*); 113.58 (*d*); 116.58 (*d*); 117.54 (*s*); 129.30 (*d*); 156.08 (*s*); 158.68 (*s*); 162.26 (*s*); 166.81 (*s*). FAB-MS (neg. mode; glycerin): 387 (26, $[M - Na]^-$), 197 (16), 153 (21), 151 (14).

N-*Benzyl (Benzylamino β-*D*-Glucopyranosid)uronamide* (**56**). A soln. of **54**/**55** (100 g, 0.57 mol) in H_2O (500 ml) was treated at 0° with $BnNH_2$ (250 ml, 2.27 mol), stirred for 6 h, and filtered. The precipitate was dried: 119 g (57%) of **56**. Colourless crystals. M.p. 144.0–146.0°. IR (KBr): 3379*s*, 3322*m*, 3203*s*, 3027*m*, 1655*s*, 1572*m*, 1454*w*, 1386*w*, 1110*w*, 1091*s*, 698*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO/D_2O): 3.03 (*t*, *J* = 8.8), 3.18 (*t*, *J* = 8.3), 3.37 (*t*, *J* = 9.2, H–C(2), H–C(3), H–C(4)); 3.39 (*d*, *J* = 9.6, H–C(5)); 3.80 (*d*, *J* = 9.3, H–C(1)); 3.87 (*t*, *J* ≈ 11.0, PhCH_2); 4.30 (br. *s*, PhCH_2); 7.19–7.36 (*m*, 10 arom. H). ^{13}C-NMR (50 MHz, (D_6)DMSO): 41.41 (*t*); 48.25 (*t*); 71.30 (*d*); 72.82 (*d*); 76.07 (*d*); 76.70 (*d*); 90.41 (*d*); 126.03–127.81 (several *d*); 138.81 (*s*); 140.48 (*s*); 169.06 (*s*). FAB-MS: 373 (6, $[M + 1]^+$), 333 (70), 185 (95), 93 (100), 75 (43). Anal. calc. for $C_{20}H_{24}N_2O_5 \cdot 0.25\ H_2O$ (372.42·0.25 H_2O): C 63.73, H 6.55, N 7.43; found: C 63.70, H 6.66, N 7.23.

*1,2,3,4-Tetra-*O*-acetyl-*N*-benzyl-α/β-*D*-glucopyranuronamides* (**57**/**58**). A suspension of **56** (100 g, 265 mmol) in H_2O (1 l) was treated with *Amberlite*® *IR-120* (250 g), stirred vigorously for 4 h, filtered, and evaporated. A soln. of the residue (50 g) in pyridine (500 ml) and Ac_2O (220 ml) was stirred for 14 h and evaporated. FC (1 kg of SiO_2, hexane/AcOEt 7:3 → 1:1) gave **57**/**58** 3:2 (68.6 g, 57%). Colourless crystals. M.p. 130.8–131.2° (Et_2O/CH_2Cl_2). R_f (hexane/AcOEt 1:1) 0.34. IR ($CHCl_3$): 3430*m*, 3008*m*, 2944*w*, 1760*s*, 1686*s*, 1604*w*, 1529*m*, 1455*w*, 1430*w*, 1370*s*, 1078*s*, 1041*s*, 912*w*, 602*w*. ^{1}H-NMR (300 MHz, $CDCl_3$) of **57**/**58** 3:2: 2.03–2.19 (several *s*, 4 AcO); 4.13 (*d*, *J* = 9.5, 0.4 H), 4.36 (*d*, *J* = 10.2, 0.6 H, H–C(5)); 4.32–4.52 (*m*, PhCH_2); 5.04 (*dd*, *J* = 10.1, 3.7, 0.6 H, H–C(2)); 5.10 (*t*, *J* = 8.5, 0.4 H); 5.22 (*t*, *J* = 9.7, 0.6 H); 5.25 (*t*, *J* = 9.3, 0.4 H); 5.32 (*t*, *J* = 8.9, 0.4 H); 5.55 (*t*, *J* = 9.8, 0.6 H); 5.76 (*d*, *J* = 8.0, 0.4 H), 6.34 (*d*, *J* = 3.7, 0.6 H, H–C(1)); 6.53–6.65 (*m*, NH); 7.27–7.39 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 20.44–20.82 (8*q*); 43.04 (*t*); 43.10 (*t*); 68.95 (*d*); 69.00 (2*d*); 69.17 (*d*); 70.23 (*d*); 70.41 (*d*); 71.98 (*d*); 73.02 (*d*); 88.30 (*d*, C(1)(**57**)); 91.33 (*d*, C(1)(**58**)); 127.72–128.78 (several *d*); 137.39 (*s*); 137.44 (*s*); 165.85 (*s*); 166.32 (2*s*); 168.75 (2*s*); 169.26 (*s*); 169.72 (2*s*); 169.85 (2*s*). EI-MS: 451 (6, M^+), 91 (80), 78 (23), 43 (100), 28 (17). Anal. calc. for $C_{21}H_{25}NO_{10}$ (451.43): C 55.87, H 5.38, N 3.10; found: C 55.86, H 5.44, N 3.04.

*(5*R*)-1,2,3,4-Tetra-*O*-acetyl-5-*C*-(1-benzyl-1*H*-tetrazol-5-yl)-α/β-*D*-xylopyranoses* (**59**/**60**). A suspension of **57**/**58** (9.00 g, 19.94 mmol) and NaN_3 (1.56 g, 24.00 mmol) in MeCN (60 ml) was treated with Tf_2O (4.90 ml, 29.85 mmol) at −20°, warmed to *ca.* 22°, and stirred until all material had dissolved (1 h). After cooling to *ca.* 0°, ^{i}Pr_2EtN (6.1 ml, 23.95 mmol) was added. The mixture was stirred for 12 h at *ca.* 22°. After the addition of ^{i}Pr_2EtN (2.0 ml, 11.68 mmol), the mixture was heated to 50° for 3 h, cooled to 0°, and treated with a sat. aq. $NaHCO_3$ soln. (300 ml) and CH_2Cl_2 (300 ml). Shaking, phase separation, extraction of the org. phase with CH_2Cl_2 (2 × 100 ml), washing of the combined org. phases with 1M H_2SO_4 and a half-sat. aq. $NaHCO_3$ soln., drying ($MgSO_4$), and evaporation gave a black tar which was subjected to FC (400 g of SiO_2, hexane/AcOEt 2:1) to give **59**/**60** 3:2 (5.80 g, 61%) as a yellow foam. An anal. sample was separated by HPLC (hexane/AcOEt 3:1). M.p. 176.5–178.0° (Et_2O/AcOEt). R_f (hexane/AcOEt 1:1) 0.41. UV (1.2%, $CHCl_3$): 263 (2.72), 258 (2.79), 252 (2.72), 201 (1.52), 199 (1.39), 194 (1.03). IR ($CHCl_3$): 3008*m*, 2399*w*, 1761*s*, 1498*w*, 1458*w*, 1428*w*, 1371*m*, 1141*w*, 1077*m*, 1047*s*, 1013*w*, 940*m*. FAB-MS (3-NOBA): 477 (54, $[M + 1]^+$), 417 (59), 315 (61), 137 (25), 91 (100). Anal. calc. for $C_{21}H_{24}N_4O_9$ (476.44): C 52.94, H 5.08, N 11.76; found: C 52.88, H 4.80, N 11.79.

Data of **59**: ^{1}H-NMR (300 MHz, $CDCl_3$): 1.94, 2.02, 2.04, 2.17 (4*s*, 4 AcO); 5.00 (*dd*, *J* = 10.4, 3.7, H–C(2)); 5.05 (*t*, *J* = 10.2, H–C(4)); 5.29 (*d*, *J* = 10.3, H–C(5)); 5.53 (*t*, *J* = 9.9, H–C(3)); 5.61 (*d*, *J* = 15.2), 5.71 (*d*, *J* = 15.1, PhCH_2); 6.42 (*d*, *J* = 3.7, H–C(1)); 7.22–7.44 (*m*, 5 arom. H). ^{13}C-NMR (125 MHz, $CDCl_3$): 20.40 (*q*);

20.41 (*q*); 20.59 (*q*); 20.78 (*q*); 52.31 (*t*); 65.80 (*d*); 68.70 (*d*); 68.77 (*d*); 69.17 (*d*); 88.75 (*d*); 127.92 (2*d*); 129.07 (*d*); 129.23 (2*d*); 133.23 (*s*); 149.90 (*s*); 168.52 (*s*); 169.03 (*s*); 169.61 (*s*); 169.93 (*s*).

Data of **60**: ^{1}H-NMR (300 MHz, $CDCl_3$): 1.92, 2.03, 2.07, 2.10 (4*s*, 4 AcO); 4.90 (*d*, J = 9.7, H–C(5)); 5.21 (*t*, $J \approx 8.7$, H–C(2)); 5.32 (*t*, J = 9.2, H–C(3)); 5.43 (*t*, J = 9.5, H–C(4)); 5.59 (*d*, J = 15.2), 5.71 (*d*, J = 15.1, PhCH_2); 5.80 (*d*, J = 8.1, H–C(1)); 7.29–7.41 (*m*, 5 arom. H). ^{13}C-NMR (100 MHz, $CDCl_3$): 20.47 (*q*); 20.53 (2*q*); 20.64 (*q*); 51.81 (*t*); 67.66 (*d*); 68.82 (*d*); 69.51 (*d*); 72.00 (*d*); 92.14 (*d*, C(1)); 128.05 (2*d*); 129.06 (*d*); 129.17 (2*d*); 133.12 (*s*); 149.57 (*s*); 168.96 (*s*); 169.04 (2*s*); 170.04 (*s*).

*(5*R*)-2,3,4-Tri-*O*-acetyl-5-*C*-(1-benzyl-1*H*-tetrazol-5-yl)-α/β-*D*-xylopyranoses* (**61**/**62**). A soln. of **59**/**60** 3:2 (300 mg, 0.63 mmol) in DMF (10 ml) was treated with $(NH_4)_2CO_3$ (150 mg, 0.63 mmol), stirred for 6 h, and poured on ice. Acidification and extraction (4 × CH_2Cl_2), washing of the combined org. phases with aq. $NaHCO_3$ soln. and H_2O, drying ($MgSO_4$), evaporation, and FC (hexane/AcOEt 1:1) gave **61**/**62** 15:1 (195 mg, 71%). Colourless crystals. M.p. 174–177° (dec., CH_2Cl_2/hexane). R_f (hexane/AcOEt 3:2) 0.38. $[\alpha]_D^{25}$ = +85.3 (*ca.* 10 min) → 61.7 (72 h) (*c* = 0.87, $CHCl_3$). IR ($CHCl_3$): 3604*w*, 3362*w*, 3008*w*, 1755*s*, 1602*m*, 1457*w*, 1428*w*, 1369*m*, 1160*w*, 1049*s*, 978*w*, 929*w*, 877*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; **61**/**62** 15:1): 1.90, 2.01, 2.10 (3*s*, AcO); 3.42 (br. *s*, disappears on addition of CD_3OD, OH); 4.87 (*dd*, J = 10.2, 3.6, H–C(2)); 5.12 (*dd*, J = 10.3, 9.4, H–C(4)); 5.46 (*dd*, J = 10.3, H–C(5)); 5.53 (br. *s*, addition of CD_3OD → *d*, J = 3.6, H–C(1)); 5.61 (*t*, $J \approx 9.7$, H–C(3)); 5.61 (*d*, J = 15.0), 5.69 (*d*, J = 15.0, PhCH_2); 7.26–7.46 (5 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$; **61**/**62** 15:1): 20.42 (*q*); 20.67 (*q*); 20.71 (*q*); 52.29 (*t*); 62.79 (*d*); 68.83 (*d*); 69.78 (*d*); 70.73 (*d*); 90.45 (*d*); 128.30–129.10 (several *d*); 133.24 (*s*); 150.67 (*s*); 169.37 (*s*); 169.91 (*s*); 170.19 (*s*). FAB-MS (3-NOBA): 435 (5, $[M + 1]^+$), 136 (40), 91 (66), 73 (78), 55 (100). Anal. calc. for $C_{19}H_{22}N_4O_8$ (434.40): C 52.53, H 5.10, N 12.90; found: C 52.55, H 4.90, N 12.84.

*(5*R*)-2,3,4-Tri-*O*-acetyl-5-*C*-(1-benzyl-1*H*-tetrazol-5-yl)-α/β-*D*-xylopyranosyl Trichloroacetimidates* (**63**/**64**). A soln. of **61**/**62** 15:1 (100 mg, 0.23 mmol) in CH_2Cl_2 (5 ml) was treated with Cl_3CCN (0.3 ml, 2.3 mmol) and a suspension (60%) of NaH in oil (6.2 mg, 0.15 mmol), stirred for 2 h, filtered through SiO_2 (5 g, elution with hexane/AcOEt 1:1), and evaporated: **63**/**64** 3:2 (103 mg, 75%). Yellow foam. R_f (hexane/AcOEt 1:1): 0.38 (**63**), 0.32 (**64**). IR ($CHCl_3$): 3345*w*, 2959*w*, 1759*s*, 1678*m*, 1498*w*, 1458*w*, 1430*w*, 1370*m*, 1291*m*, 1141*m*, 1115*m*, 1044*s*, 973*m*, 939*m*, 911*m*, 833*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; **63**/**64** 3:2): 1.93–2.05 (several *s*, 3 AcO); 5.06 (*d*, J = 9.4, 0.4 H, H–C(5)); 5.06 (*dd*, J = 10.3, 3.7, 0.6 H, H–C(2)); 5.23–5.43 (*m*, 2 H); 5.55–5.75 (*m*, 3 H); 6.00 (*d*, J = 7.8, 0.4 H), 6.65 (*d*, J = 3.7, 0.6 H, H–C(1)); 7.22–7.43 (*m*, 5 arom. H); 8.80 (*s*, 0.6 H), 8.83 (*s*, 0.4 H, NH). ^{13}C-NMR (75 MHz, $CDCl_3$; **63**/**64** 3:2): signals of **63**: 20.43–20.66 (several *q*); 51.91 (*t*); 65.39 (*d*); 68.80 (*d*); 69.12 (*d*); 69.24 (*d*); 90.31 (*s*); 92.63 (*d*); 127.89–129.18 (several *d*); 133.21 (*s*); 149.95 (*s*); 160.68 (*s*); 168.81–170.02 (several *s*); signals of **64**: 67.90 (*d*); 68.85 (*d*); 69.34 (*d*); 71.55 (*d*); 89.96 (*s*); 95.63 (*d*); 149.47 (*s*); 160.82 (*s*). FAB-MS (3-NOBA): 580 (12), 578 (12, $[M + 1]^+$), 417 (7), 418 (34), 417 (100, $[M - OC(NH)CCl_3]^+$), 315 (31).

*4-Methyl-2-oxo-2*H*-1-benzopyran-7-yl (5*R*)-2,3,4-Tri-O-acetyl-5-C-(1-benzyl-1*H*-tetrazol-5-yl)-β-D-xylopyranoside* (**65**). A mixture of 3-Å molecular sieves, 4-methyl-7-(trimethylsilyloxy)-2*H*-1-benzopyran-2-one (90 mg, 0.35 mmol) [49] and **63**/**64** (154 mg, 0.27 mmol) was dissolved in CH_2Cl_2 (0.5 ml), treated with a soln. of $BF_3 \cdot Et_2O$ (25 µl, 0.19 mmol) in CH_2Cl_2 (0.5 ml), stirred at −20° for 30 min, warmed to 23°, stirred for 1 h, cooled to −20°, treated with pyridine (1.5 ml) and Ac_2O (0.3 ml), warmed to 23°, stirred for 45 min, filtered through *Hyflo Super Cel*®, and evaporated. FC (hexane/AcOEt 1:1) yielded 75% (118 mg) of **65**. Colourless crystals. M.p. 226.0–228.0° (CH_2Cl_2/hexane). R_f (hexane/AcOEt 2:3) 0.41. $[\alpha]_D^{25}$ = −12.4 (*c* = 0.77, $CHCl_3$). IR ($CHCl_3$): 3008*w*, 1759*s*, 1615*m*, 1426*w*, 1388*m*, 1369*m*, 1161*m*, 1070*m*, 1043*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.92, 2.03, 2.10 (3*s*, 3 AcO); 2.40 (*s*, Me); 5.05 (*dd*, J = 9.9, 9.4, H–C(4)); 5.19 (*d*, J = 10.0, H–C(5)); 5.32 (*dd*, J = 9.3, 7.7, H–C(2)); 5.37 (*d*, J = 7.6, H–C(1)); 5.44 (*t*, J = 9.4, H–C(3)); 5.57 (*d*, J = 14.9), 5.67 (*d*, J = 14.9, PhCH_2); 6.21–6.22 (*m*, H–C(3′)); 6.83–6.85 (*m*, H–C(5′), H–C(6′)); 7.17–7.26 (*m*, 5 arom. H); 7.47–7.50 (*m*, H–C(8′)). ^{13}C-NMR (125 MHz, $CDCl_3$): 18.67 (*q*); 20.33 (*q*); 20.52 (*q*); 20.57 (*q*); 52.47 (*t*); 68.55 (*d*); 69.06 (*d*); 70.66 (*d*); 71.09 (*d*); 98.91 (*d*); 104.67 (*d*); 113.32 (*d*); 113.69 (*d*); 116.14 (*s*); 126.04 (*d*); 128.16 (2*d*); 128.89 (*d*); 128.92 (2*d*); 133.01 (*s*); 149.36 (*s*, C(5′)); 151.89 (*s*); 154.75 (*s*); 158.49 (*s*); 160.45 (*s*); 169.18 (2*s*); 169.80 (*s*). FAB-MS (3-NOBA): 594 (7), 593 (22, $[M + 1]^+$), 307 (30), 154 (100), 137 (85), 123 (27), 107 (41), 91 (60), 69 (80). Anal. calc. for $C_{29}H_{28}N_4O_{10}$ (592.56): C 58.78, H 4.76, N 9.46; found: C 58.63, H 4.65, N 9.40.

*4-Methyl-2-oxo-2*H*-1-benzopyran-7-yl (5*R*)-5-C-(1-Benzyl-1*H*-tetrazol-5-yl)-β-D-xylopyranoside* (**66**). A soln. of **65** (150 mg, 0.25 mmol) in MeOH (3 ml) was treated with 0.2M NaOMe in MeOH (0.5 ml), stirred for 90 min, neutralized with *Amberlite® IR-120*, and evaporated. Crystallization in ^{i}PrOH gave **66** (89 mg, 76%). M.p. 175.0–176.0°. R_f (AcOEt/MeOH/H_2O 7:2:1) 0.70. IR (KBr): 3384*s*, 2919*m*, 1721*s*, 1613*s*, 1562*m*, 1456*m*, 1391*s*, 1268*s*, 1075*s*, 853*m*, 808*w*, 724*m*. ^{1}H-NMR (300 MHz, CD_3OD): 2.40 (br. *s*, Me); 3.63–3.71 (*m*, 2 H); 3.91–3.97 (*m*, 1 H); 5.11 (*d*, J = 9.7, H–C(5)); 5.37 (*d*, J = 7.5, H–C(1)); 5.71 (*s*, PhCH_2); 6.17 (*d*, J = 1.2, H–C(3′)); 6.94–6.98 (*m*, H–C(6′), H–C(8′)); 7.11–7.18 (*m*, 5 arom. H); 7.55–7.58 (*m*, H–C(6′)). ^{13}C-NMR (125 MHz, CD_3OD): 18.65 (*q*); 52.22 (*t*); 69.72 (*d*); 73.51 (*d*); 74.30 (*d*); 77.10 (*d*); 101.35 (*d*); 104.65 (*d*); 113.15 (*d*); 114.90 (*d*); 116.36 (*s*);

127.42 (*d*); 128.68 (2*d*); 129.44 (*d*); 129.79 (2*d*); 135.64 (*s*); 154.13 (*s*); 155.31 (*s*); 155.96 (*s*); 161.21 (*s*); 163.16 (*s*). FAB-MS (3-NOBA): 467 (72, $[M + 1]^+$), 154 (100), 91 (93). Anal. calc. for $C_{23}H_{22}N_4O_7$ (466.45): C 59.22, H 4.75, N 12.01; found: C 58.35, H 4.76, N 11.72.

*4-Methyl-2-oxo-2*H*-1-benzopyran-7-yl (5*R*)-5-*C*-(Tetrazol-5-yl)-β-*D*-xylopyranoside* (**5**). A soln. of **66** (82 mg, 0.18 mmol) in MeOH (3 ml) was treated with HCO_2H (0.6 ml) and 10% Pd/C (20 mg), stirred for 6 h, treated with HCO_2H (0.4 ml) and 10% Pd/C (8 mg), stirred for 7 h, filtered, and evaporated: **5** (65 mg, 98%). R_f (AcOEt/MeOH/H_2O 7:2:1) 0.30. IR (KBr): 3409*s*, 2919*m*, 1718*s*, 1611*s*, 1560*m*, 1507*w*, 1426*m*, 1391*s*, 1370*m*, 1277*s*, 1207*m*, 1165*m*, 1073*s*, 1020*s*, 851*w*, 808*w*. ^{1}H-NMR (500 MHz, CD_3OD): 2.42 (br. *s*, Me); 3.65–3.78 (*m*, 3 H); 5.05 (*d*, J = 9.7, H–C(5)); 5.34 (*d*, J = 7.7, H–C(1)); 6.19 (*d*, J = 1.2, H–C(3′)); 7.05–7.10 (*m*, 2 H); 7.68 (*d*, H–C(6′)). ^{13}C-NMR (125 MHz, CD_3OD): 18.66 (*q*); 70.89 (*d*); 74.15 (*d*); 74.57 (*d*); 77.19 (*d*); 102.03 (*d*); 105.10 (*d*); 113.14 (*d*); 114.82 (*d*); 116.43 (*s*); 127.47 (*d*); 155.43 (*s*); 156.05 (*s*); 156.61 (*s*); 161.64 (*s*); 163.27 (*s*). FAB-MS (3-NOBA): 753 (14, $[2M + 1]^+$), 377 (62, $[M + 1]^+$), 307 (30), 177 (100), 154 (83), 137 (69), 107 (37), 81 (53).

*Benzyl (1,2,3,4-Tetra-*O*-acetyl-α/β-*D*-glucopyran)uronates* (**69**/**70**). A soln. of **67**/**68**·H_2O (2.00 g, 8.54 mmol) in DMF (30 ml) was treated with BnBr (1.5 ml, 12.6 mmol), stirred at *ca.* 23° for 24 h, filtered through *Hyflo Super Cel*®, and treated with Ac_2O (20 ml) and pyridine (40 ml) at *ca.* 23° for 14 h. Usual workup ($CHCl_3$, washing with H_2O, H_2SO_4, and $NaHCO_3$ soln.) and FC (80 g of SiO_2) gave **69**/**70** 1:1 (1.90 g, 49%). An anal. sample was crystallized in Et_2O. Colourless crystals. M.p. 137.5–139.5°. R_f (hexane/AcOEt 2:1) 0.17. IR ($CHCl_3$): 2961*w*, 1761*s*, 1499*w*, 1456*w*, 1429*w*, 1369*m*, 1091*m*, 1041*m*, 913*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.77 (1.5 H), 1.80 (1.5 H); 2.00 (3.0 H), 2.02 (1.5 H), 2.03 (1.5 H), 2.09 (1.5 H), 2.17 (1.5 H, 4 AcO); 4.22 (*d*, J = 9.6, 0.5 H), 4.45 (*d*, J = 10.0, 0.5 H, H–C(5)); 5.09–5.29 (*m*, 4.5 H); 5.49 (*t*, $J \approx 9.9$, 0.5 H); 5.77 (*d*, J = 7.6, 0.5 H), 6.40 (*d*, J = 3.7, 0.5 H, H–C(1)); 7.32–7.39 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 20.25–20.82 (several *q*); 68.01 (2*t*); 68.87 (2*d*); 69.06 (*d*); 69.15 (*d*); 70.20 (*d*); 70.49 (*d*); 71.94 (*d*); 73.01 (*d*); 88.79 (*d*); 91.35 (*d*); 128.35–128.84 (several *d*); 134.55 (2*s*); 166.33 (*s*); 166.74 (*s*); 168.47 (*s*); 168.83 (*s*); 169.17 (*s*); 169.33 (2*s*); 169.52 (*s*); 169.89 (*s*); 170.00 (*s*). FAB-MS (3-NOBA): 475 (6, $[M + Na]^+$), 394 (24), 393 (100, $[M - OAc]^+$), 193 (48), 154 (22), 137 (57), 136 (29), 106 (25). Anal. calc. for $C_{21}H_{24}O_{11}$ (452.41): C 55.75, H 5.35; found: C 55.66, H 5.41.

*Benzyl (2,3,4-Tri-*O*-acetyl-α/β-*D*-glucopyran)uronates* (**71**/**72**). A soln. of **69**/**70** 1:1 (6.35 g, 14.04 mmol) in DMF (100 ml) was treated with $(NH_4)_2CO_3$ (3.18 g) at *ca.* 22° for 4 h, cooled to 5°, and treated with CH_2Cl_2 (200 ml) and ice (*ca.* 400 ml). Extraction with CH_2Cl_2, washing of the combined org. phases with 0.5M H_2SO_4 and sat. aq. $NaHCO_3$ soln., drying ($MgSO_4$), evaporation, and FC (hexane/AcOEt 1:1) gave **71**/**72** 4:1 (3.85 g, 67%). Colourless oil. R_f (hexane/AcOEt 1:2) 0.44. IR ($CHCl_3$): 3594*w*, 2960*w*, 1754*s*, 1498*w*, 1456*w*, 1429*w*, 1369*m*, 1146*w*, 1065*m*, 1040*m*, 908*w*. ^{1}H-NMR (200 MHz, $CDCl_3$; **71**/**72**): signals of **71**: 1.77, 2.01, 2.08 (3*s*, 3 AcO); 3.50 (br. *s*, *ca.* 1 H, exchange with CD_3OD, OH); 4.62 (*d*, J = 10.1, H–C(5)); 4.92 (*dd*, J = 10.1, 3.6, H–C(2)); 5.10 (*d*, J = 12.0), 5.19 (*d*, J = 12,0, PhCH_2); 5.20 (*t*, $J \approx 10.1$, H–C(4)); 5.55 (*d*, $J \approx 3.6$, addition of $CD_3OD \rightarrow$ shift to higher fields by 0.13 ppm, H–C(1)); 5.56 (*t*, $J \approx 9.7$, H–C(3)); 7.35 (*s*, 5 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$; **71**/**72** 4:1): signals of **71**: 20.30–20.67 (several *q*); 67.95 (*t*); 67.98 (*d*); 69.30 (*d*); 69.50 (*d*); 70.74 (*d*); 90.19 (*d*); 128.66–128.86 (several *d*); 134.59 (*s*); 168.13 (*s*); 169.69 (*s*); 170.12 (*s*); 170.24 (*s*); signals of **72**: 20.30–20.67 (several *q*); 68.07 (*t*); 69.34 (*d*); 71.76 (*d*); 72.54 (*d*); 72.75 (*d*); 95.45 (*d*); 128.66–128.86 (several *d*); 134.52 (*s*); 167.17–170.45 (several *s*). FAB-MS (3-NOBA): 433 (11, $[M + Na]^+$), 394 (17), 393 (76, $[M - OH]^+$), 307 (19), 303 (13), 289 (14), 193 (29), 155 (38), 154 (100).

*Benzyl (*E*/*Z*)-2,3,4-Tri-*O*-acetyl-*D*-glucuronate 1-Oximes* (**73**/**74**). A soln. of **71**/**72** 4:1 (3.85 g, 9.38 mmol) in pyridine (55 ml) was treated with $NH_2OH \cdot HCl$ (1.96 g, 28.2 mmol) at *ca.* 23° for 2.5 h, diluted with CH_2Cl_2 and H_2O, and shaken. Washing of the org. layer with 0.5M H_2SO_4 and sat. aq. $NaHCO_3$ soln., drying ($MgSO_4$), and evaporation gave crude **73**/**74** 7:3 (3.45 g, 86%) which was used for the next step. Yellow foam. R_f (hexane/AcOEt 1:2): 0.35 (**73**), 0.29 (**74**). IR ($CHCl_3$): 3573*w*, 3038*w*, 1751*s*, 1498*w*, 1456*w*, 1428*w*, 1373*m*, 1086*m*, 1045*m*, 958*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; **73**/**74** 7:3): 1.85, 1.86, 2.05, 2.09, 2.09, 2.10 (6*s*, 3 AcO); 3.43 (br. *s*, exchange with CD_3OD, OH–C(5)); 4.21 (*d*, J = 7.4, 0.7 H), 4.23 (*d*, J = 6.3, 0.3 H, H–C(5)); 5.11 (*d*, J = 11.9, 0.7 H), 5.20 (*d*, $J \approx 12.1$, 0.7 H); 5.14 (*d*, J = 12.0, 0.3 H), 5.22 (*d*, $J \approx 12.7$, 0.3 H, PhCH_2); 5.22 (*dd*, $J \approx 6.3$, 5.1, 0.3 H), 5.23 (*dd*, J = 7.4, 3.5, 0.7 H, H–C(4)); 5.56 (*dd*, J = 7.1, 5.8, 0.7 H), 6.14 (*t*, J = 5.7, 0.3 H, H–C(2)); 5.67 (*dd*, J = 7.1, 3.5, 0.7 H), 5.76 (*dd*, J = 5.6, 4.7, 0.3 H, H–C(3)); 6.55 (*d*, J = 5.8, 0.3 H), 7.29 (*d*, J = 5.8, 0.7 H, H–C(1)); 7.33–7.40 (*m*, 5 arom. H); 8.34 (br. *s*, exchange with CD_3OD, 0.7 H), 8.55 (br. *s*, exchange with CD_3OD, 0.3 H, NOH). ^{13}C-NMR (125 MHz, $CDCl_3$; **73**/**74** 7:3): signals of **73**: 20.47–20.64 (several *q*); 68.55 (*t*); 68.95 (*d*); 69.34 (*d*); 69.81 (*d*); 71.11 (*d*); 128.68–129.05 (several *d*); 134.37 (*s*); 145.50 (*d*); 169.60 (*s*); 169.81 (*s*); 170.20 (*s*); 171.81 (*s*); signals of **74**: 65.65 (*d*); 68.55 (*t*); 69.25 (*d*); 69.42 (*d*); 71.79 (*d*); 134.46 (*s*); 146.41 (*d*); 169.63 (*s*); 169.85 (*s*); 170.34 (*s*); 171.63 (*s*). FAB-MS (3-NOBA): 427 (26), 426 (100, $[M + 1]^+$), 366 (22).

*(*Z*)-2,3,4-Tri-*O*-acetyl-*D*-glucarhydroximo-1,5-lactone 6-Benzyl Ester* (**75**). A soln. of crude **73**/**74** 7:3 (3.15 g, *ca.* 7.41 mmol) in CH_2Cl_2 (100 ml) was treated with DBU (1.36 g, 8.93 mmol) and NCS (1.19 g, 8.91 mmol) at −78°,

and allowed to warm to *ca.* 23° within 30 min. Addition of CH_2Cl_2 and H_2O, shaking, phase separation, drying of the org. phase ($MgSO_4$), and FC (100 g of SiO_2, hexane/AcOEt 2:1) gave **75** (2.40 g, 77% from **71/72**). Hygroscopic foam. R_f (hexane/AcOEt 1:2) 0.33. IR ($CHCl_3$): 3573*w*, 1760*s*, 1680*w*, 1498*w*, 1456*w*, 1372*m*, 1145*w*, 1097*w*, 1053*m*, 963*w*, 909*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.91, 2.03, 2.13 (3*s*, 3 AcO); 4.97 (*d*, J = 5.5, H–C(5)); 5.18 (*t*, $J \approx 3.7$, H–C(3)); 5.22 (*d*, J = 12.1), 5.28 (*d*, $J \approx 12.7$, PhCH_2); 5.30 (*s*, addition of $CD_3OD \rightarrow$ partial exchange, OH); 5.36 (*dd*, $J \approx 5.0$, 4.2, H–C(4)); 5.49 (*d*, J = 3.9, H–C(2)); 7.36–7.40 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz, C_6D_6): 19.87 (*q*); 20.03 (*q*); 20.16 (*q*); 66.73 (*d*); 68.04 (*t*); 69.70 (*d*); 70.69 (*d*); 75.23 (*d*); 128.75 (*d*); 128.87 (2*d*); 128.94 (2*d*); 135.34 (*s*); 147.53 (*s*); 166.76 (*s*); 168.67 (*s*); 168.97 (*s*); 169.05 (*s*). FAB-MS (3-NOBA): 426 (6), 425 (25), 424 (100, $[M + 1]^+$), 307 (16). Anal. calc. for $C_{19}H_{21}NO_{10}$ (423.37): C 53.90, H 5.00, N 3.31; found: C 53.37, H 5.40, N 3.39.

*(Z)-2,3,4-Tri-*O*-acetyl-*N*-[(phenylamino)carbonyloxy]-*D*-glucarimido-1,5-lactone 6-Benzyl Ester* (**76**). A soln. of **75** (500 mg, 1.18 mmol) in CH_2Cl_2 (20 ml) was treated with PhNCO (0.25 ml, 2.29 mmol) and ^{i}Pr$_2$EtN (30 µl, 0.18 mmol) at 0°, immediately allowed to warm to 23°, and stirred for 30 min. Evaporation and FC gave **76** (492 mg, 77%). Foam. R_f (hexane/AcOEt 1:1) 0.36. $[\alpha]_D^{25} = +15.4$ (c = 1.14, $CHCl_3$). IR ($CHCl_3$): 3393*w*, 3038*w*, 1762*s*, 1670*w*, 1602*w*, 1523*m*, 1445*m*, 1372*m*, 1312*w*, 1178*m*, 1133*w*, 1101*m*, 1052*m*, 1010*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.98, 2.03, 2.18 (3*s*, 3 AcO); 5.03 (*d*, J = 5.6, H–C(5)); 5.21 (*t*, $J \approx 3.5$, H–C(3)); 5.23 (*d*, $J \approx 13.2$), 5.28 (*d*, J = 11.9, PhCH_2); 5.37 (*dd*, $J \approx 5.6$, 3.1, H–C(4)); 5.64 (*d*, J = 4.0, H–C(2)); 7.09–7.48 (*m*, 10 arom. H); 7.79 (br. *s*, NH). ^{13}C-NMR (75 MHz, $CDCl_3$): 20.43 (*q*); 20.50 (*q*); 20.66 (*q*); 65.54 (*d*); 68.50 (*t*); 68.83 (*d*); 69.64 (*d*); 75.42 (*d*); 119.31 (2*d*); 124.22 (*d*); 128.76 (2*d*); 128.82 (2*d*); 128.99 (*d*); 129.14 (2*d*); 134.18 (*s*); 136.92 (*s*); 150.57 (*s*); 150.94 (*s*); 165.80 (*s*); 168.26 (*s*); 168.59 (*s*); 168.91 (*s*). FAB-MS (3-NOBA): 545 (7), 544 (31), 543 (100, $[M + 1]^+$), 424 (22), 423 (13), 307 (30), 289 (17). Anal. calc. for $C_{26}H_{26}N_2O_{11}$ (542.50): C 57.56, H 4.83, N 5.16; found: C 57.58, H 5.01, N 5.29.

*(Z)-*N*-[(Phenylamino)carbonyloxy]-*D*-glucarimido-1,5-lactone 6-Sodium Salt* (**7**). A soln. of **76** (255 mg, 0.47 mmol) in MeOH (6 ml) was treated with H_2 (1–2 bar) in the presence of 10% Pd/C (5 mg) at *ca.* 23° for 30 min. When TLC revealed completion of the reaction (new spot at R_f (AcOEt/MeOH/H_2O 7:2:1) 0.32), a soln. of NH_3 in MeOH (3.0 ml) was added dropwise. After 3 h, the mixture was filtered through *Hyflo Super Cel*® and evaporated. The residue, **77**, was dissolved in H_2O, and filtered through a column packed with *Dowex® 50W X2* (50–100 mesh, Na^+ form). The fractions containing crude **7** were collected and poured on a column packed with *LiChroprep® RP-18* (40–63 µm). Elution with H_2O, lyophilization, precipitation from MeOH with EtOH, and lyophilization gave **7** (141 mg, 86%). R_f 0.47. IR (KBr; **7**): 3380*s*, 1751*m*, 1620*s*, 1550*m*, 1501*w*, 1447*m*, 1406*w*, 1318*w*, 1254*w*, 1211*m*, 1110*w*, 1062*w*, 1020*m*, 753*w*. ^{1}H-NMR (200 MHz, CD_3OD; **77**): 3.73 (*dd*, J = 7.0, 4.9, H–C(4)); 4.02 (*t*, $J \approx 5.5$, H–C(3)); 4.40 (*d*, J = 7.2, H–C(5)); 4.56 (*d*, J = 6.1, H–C(2)); 7.01–7.09 (*m*, 1 arom. H); 7.25–7.33 (*m*, 2 arom. H); 7.42–7.52 (*m*, 2 arom. H). ^{13}C-NMR (50 MHz, CD_3OD; **77**): 70.73 (*d*); 75.07 (*d*); 77.66 (*d*); 82.21 (*d*); 120.60 (*d*); 124.92 (2*d*); 130.21 (2*d*); 139.79 (*s*); 155.52 (*s*); 161.00 (*s*); 174.92 (*s*). FAB-MS (neg. mode; glycerin; **7**): 325 (32, $[M - Na^+]^-$), 183 (100), 181 (41).

*(5R,E/Z)-2,3,4-Tri-*O*-acetyl-5-*C*-[bis(benzyloxy)phosphoryl]-*D*-xylose Oxime* (**78/79**). A soln. of **48/49** (500 mg, 0.932 mmol) in pyridine (12.5 ml) was treated with $NH_2OH \cdot HCl$ (195 mg, 2.81 mmol) at *ca.* 23° for 4 h, diluted with CH_2Cl_2 and H_2O, and shaken. Washing of the org. layer with 0.5M H_2SO_4 and sat. aq. $NaHCO_3$ soln., drying ($MgSO_4$), and evaporation gave crude **78/79** (487 mg, 95%) which immediately was used for the next step. Yellow oil. R_f (hexane/AcOEt 1:4): 0.24 (**78**), 0.19 (**79**). IR ($CHCl_3$): 3574*w*, 3249*m*, 3093*w*, 3069*w*, 3008*w*, 2959*w*, 1751*s*, 1603*w*, 1498*w*, 1456*m*, 1431*w*, 1373*s*, 1041*s*, 998*s*, 967*m*, 869*w*, 601*m*. ^{1}H-NMR (500 MHz, C_6D_6; **78/79** 3:1): signals of **78**: see *Tables 1* and *2*; 1.56, 1.66, 1.70 (3*s*, 3 AcO); 4.96 (*dd*, J = 11.6, 7.3), 5.00 (*dd*, J = 11.7, 8.3, PhCH_2); 5.04–5.10 (*m*, PhCH_2); 6.99–7.31 (*m*, 10 arom. H); 7.62 (*d*, J = 5.4, H–C(1)); 11.10 (br. *s*, exchange with CD_3OD, NOH); signals of **79**: see *Tables 1* and *2*; 10.70 (br. *s*, exchange with CD_3OD, NOH). ^{13}C-NMR (125 MHz, C_6D_6; **78/79**): signals of **78**: see *Table 3*; 20.15 (*q*); 20.30 (*q*); 20.34 (*q*); 68.93 (*dt*, J(P,C) = 7.1); 69.42 (*dt*, J(P,C) = 7.2); 127.53–128.85 (several *d*); 136.47 (*d*, J(P,C) = 6.2); 136.59 (*d*, J(P,C) = 5.7); 169.22 (*s*); 169.47 (*s*); 169.80 (*s*); signals of **79**: 146.81 (*d*, C(1)). FAB-MS (3-NOBA): 552 (8, $[M + 1]^+$), 189 (8), 181 (9), 171 (23), 170 (100), 136 (29).

*(5R,Z)-2,3,4-Tri-*O*-acetyl-5-*C*-[bis(benzyloxy)phosphoryl]-*D*-xylonhydroximo-1,5-lactone* (**80**). A soln. of crude **78/79** (300 mg, *ca.* 0.54 mmol) in CH_2Cl_2 (12 ml) was treated with a soln. of DBU (95 mg, 0.62 mmol) in CH_2Cl_2 (3 ml) and NCS (84 mg, 0.63 mmol) at −78°, and allowed to warm to *ca.* 23° within 30 min. Addition of CH_2Cl_2 and H_2O, shaking, phase separation, drying of the org. phase ($MgSO_4$), and FC (30 g of SiO_2, hexane/AcOEt 1:1) gave **80** (269 mg, 88% from **48/49**). Colourless foam. R_f (hexane/AcOEt 1:2) 0.28. $[\alpha]_D^{25} = +50.2$ (c = 0.83, $CHCl_3$). IR ($CHCl_3$): 3265*w*, 3008*m*, 1754*s*, 1498*w*, 1456*m*, 1430*w*, 1374*s*, 1044*s*, 998*s*, 967*m*, 871*w*. ^{1}H-NMR (300 MHz, C_6D_6): see *Tables 1* and *2*; 1.52, 1.54, 1.63 (3*s*, 3 AcO); 5.08 (*d*, J = 8.5, PhCH_2); 5.20 (*dd*, J = 11.6, 7.2), 5.28 (*dd*, J = 11.6, 8.7, PhCH_2); 6.99–7.12 (*m*, 6 arom. H); 7.25–7.33 (*m*, 4 arom. H); 9.26 (br. *s*, exchange with CD_3OD, NOH). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; 20.39 (*q*); 20.57 (*q*); 20.69 (*q*);

69.19 (*dt*, J(P,C) = 6.7); 69.61 (*dt*, J(P,C) = 6.8); 128.35–128.77 (several *d*); 135.47 (*d*, J(P,C) ≈ 5.4); 135.55 (*d*, J(P,C) ≈ 6.1); 168.37 (*s*); 168.80 (*s*); 169.10 (*s*). ^{31}P-NMR (121 MHz, $CDCl_3$): 15.53. FAB-MS (3-NOBA): 552 (9), 551 (37), 550 (100, $[M+1]^+$), 388 (10). Anal. calc. for $C_{25}H_{28}NO_{11}P$ (549.47): C 54.65, H 5.14, N 2.55; found: C 54.37, H 5.35, N 2.33.

*(5*R,E*)-2,3,4-Tri-*O*-acetyl-5-*C*-[bis(benzyloxy)phosphoryl]-*D*-xylonhydroximo-1,5-lactone* (**81**). A soln. of crude **78**/**79** (190 mg, *ca.* 0.35 mmol) in CH_2Cl_2 (4 ml) was treated with DBU (57 µl, 0.38 mmol) and NCS (51 mg, 0.38 mmol) at *ca.* 23° for 10 min. Workup as for **80** and FC (20 g of SiO_2, hexane/AcOEt 1:2) gave **81** (130 mg, 63% from **48**/**49**). Colourless oil. R_f (hexane/AcOEt 1:2) 0.28. IR ($CHCl_3$): 3576*m*, 3312*w*, 3092*w*, 3069*w*, 3008*m*, 2963*w*, 1760*s*, 1699*m*, 1498*w*, 1456*m*, 1430*w*, 1372*s*, 1334*w*, 1248*s*, 1139*w*, 1044*s*, 1024*s*, 999*s*, 926*m*, 900*m*, 860*w*, 658*w*. ^{1}H-NMR (300 MHz, C_6D_6): see *Tables 1* and *2*; 1.43, 1.57, 1.62 (3*s*, 3 AcO); 4.89 (*dd*, J = 11.8, 7.9), 5.01 (*dd*, J = 11.8, 9.0, PhCH_2); 5.44 (*dd*, J = 11.9, 8.0), 5.51 (*dd*, J = 11.9, 9.1, PhCH_2); 6.90–7.40 (*m*, 10 arom. H); 8.94 (br. *s*, NOH). ^{13}C-NMR (50 MHz, $CDCl_3$): see *Table 3*; 20.38 (*q*); 20.76 (2*q*); 68.51 (*dt*, J(P,C) = 6.7); 69.66 (*dt*, J(P,C) = 6.4); 128.26–129.11 (several *d*); 136.01 (*d*, J(P,C) = 6.2); 136.48 (*d*, J(P,C) = 5.8); 169.00 (2*s*); 169.42 (*s*). FAB-MS (3-NOBA): 551 (24), 550 (100, $[M+1]^+$), 399 (28), 155 (32), 154 (83).

*(5*R,Z*)-2,3,4-Tri-*O*-acetyl-5-*C*-[bis(benzyloxy)phosphoryl]-*N*-[(phenylamino)carbonyloxy]-*D*-xylonimido-1,5-lactone* (**82**). A soln. of **80** (182 mg, 0.33 mmol) in CH_2Cl_2 (6 ml) was treated with PhNCO (72 µl, 0.66 mmol) and ^{i}Pr$_2$EtN (30 µl, 0.18 mmol) at 0° for 30 min. Evaporation and FC (50 g of SiO_2, hexane/AcOEt 1:1) gave **82** (217 mg, 98%). Foam. R_f (hexane/AcOEt 1:2) 0.32. $[\alpha]_D^{25}$ = +53.2 (*c* = 0.75, $CHCl_3$). IR ($CHCl_3$): 3393*w*, 3008*w*, 2964*w*, 1762*s*, 1669*m*, 1602*m*, 1522*m*, 1456*w*, 1445*m*, 1373*m*, 1311*w*, 1296*w*, 1043*s*, 1008*s*, 996*s*. ^{1}H-NMR (300 MHz, C_6D_6): see *Tables 1* and *2*; 1.49, 1.51, 1.59 (3*s*, 3 AcO); 4.99 (*dd*, J ≈ 12.0, 8.7), 5.03 (*dd*, J ≈ 11.0, 9.3, PhCH_2); 5.13 (*dd*, J = 11.5, 7.2), 5.23 (*dd*, J = 11.8, 9.3, PhCH_2); 6.80–7.45 (*m*, 15 arom. H); 7.94 (br. *s*, NH). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; 20.39 (*q*); 20.58 (*q*); 20.68 (*q*); 69.27 (*dt*, J(P,C) = 6.7); 69.72 (*d*, J(P,C) = 6.5); 119.41 (2*d*); 124.25 (2*d*); 128.31–129.14 (several *d*); 135.28 (*d*, J(P,C) ≈ 5.6); 135.36 (*d*, J(P,C) ≈ 5.8); 136.92 (*s*); 150.94 (*s*); 168.01 (*s*); 168.60 (*s*); 168.62 (*s*). FAB-MS (3-NOBA): 670 (35), 669 (100, $[M+1]^+$), 551 (20), 550 (68, $[M+1-$PhNCO$]^+$), 490 (25), 460 (21), 307 (27), 182 (20), 181 (39). Anal calc. for $C_{32}H_{33}N_2O_{12}P$ (668.59): C 57.49, H 4.97, N 4.19; found: C 57.20, H 5.15, N 4.21.

*(5*R,Z*)-N-[(Phenylamino)carbonyloxy]-5-*C*-phosphono-*D*-xylonimido-1,5-lactone Disodium Salt* (**8**). A mixture of **82** (180 mg) and 10% Pd/C (5 mg) in MeOH (6 ml) was treated with H_2 at 1 atm for 30 min (TLC: no **82** left; new spot at R_f (AcOEt/MeOH/H_2O 4:2:1) 0.50). A soln. of NH_3 in MeOH (4.5 ml) was added dropwise. After completion of the reaction (3 h), the mixture was filtered through *Hyflo Super Cel*®, evaporated, dissolved in H_2O, and filtered through a column packed with *Dowex*® *50W X2* (50–100 mesh, Na^+ form). The fractions containing crude **8** were collected and poured on a column with *LiChroprep*® *RP-18* (40–63 µm) which was eluted with H_2O. Lyophilization, precipitation from H_2O with EtOH, and lyophilization gave pure **8** (50 mg, 48%). R_f (AcOEt/MeOH/H_2O 4:2:1) 0.23. IR (KBr): 3407*s*, 1750*m*, 1654*m*, 1604*m*, 1558*m*, 1502*w*, 1447*m*, 1318*w*, 1256*w*, 1214*m*, 1082*s*, 976*m*, 907*w*. ^{1}H-NMR (400 MHz, D_2O): see *Tables 1* and *2*; 7.29–7.33 (*m*, 1 arom. H); 7.29–7.33 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, D_2O): see *Table 3*; 123.65 (2*d*); 127.64 (*d*); 132.00 (2*d*); 139.39 (*s*); 157.54 (*s*). ^{31}P-NMR (162 MHz, D_2O): −2.63. FAB-MS (neg. mode; glycerin): 361 (16 $[M-Na^+]^-$), 275 (17), 183 (100), 181 (38).

Enzyme Studies. a) *Hydrolysis of* **4**, **5** *and* **6** *by Bovine Liver β-Glucuronidase.* Measurements were performed at 25° and were started by addition of a soln. (2 mM, 38 µl) of **4**, **5**, or **6** (*Fluka*) to a soln. of NaOAc/HCl (0.1M, pH 4.5, 1 ml) and bovine liver *β-glucuronidase* (*ca.* 0.3 U/ml, 30 µl) in H_2O. The reaction was quenched after 2, 5, 10 and 30 min by addition of 0.5M NaOH (2.0 ml). The increase of emission with time indicated the hydrolysis of the substrate. Excitation wavelength was 364 nm, emission wavelength 446 nm. While with **6** an increase of emission with time was observed, there was no evidence for the hydrolysis of **4** and **5**.

b) *Inhibition of* E. coli *K 12 β-Glucuronidase* (*Fluka*, 89 U/ml) *by* **7**. The inhibition constant (K_I) was determined at 37.8° using a 0.08M NaH_2PO_4/Na_2HPO_4 buffer (pH 7.2) and 4-nitrophenyl *β*-D-glucuronide·H_2O (= (4-nitrophenyl) *β*-D-glucopyranosid)uronic acid – water; *Fluka*) as substrate. Measurements were started by addition of *E. coli β*-glucuronidase (50 µl, *ca.* 0.04 U) to the mixed solns. of the substrate (750 µl) and **7** (200 µl). The increase of absorption per minute at 400 nm was taken as the velocity for the hydrolysis of the substrate. This increase was linear during all measurements (3 min). K_M (1.6 mM) was determined by means of a *Lineweaver-Burk* plot [59] on the basis of four substrate concentrations (1.19, 0.89, 0.59 and 0.42 mM). K_I values were determined on the basis of these substrate concentrations and eight inhibitor concentrations (0, 3.6, 5.4, 7.2, 10.8, 14.4, 18.0 and 54.0 µM) by taking the slopes from all eight *Lineweaver-Burk* plots, and plotting them against the inhibitor concentrations. After fitting the data to a straight line (R = 1.00), the negative [I]-intercept of this plot gave K_I.

c) *Inhibition of the Bovine Liver β-Glucuronidase* (*Fluka*, 0.04 U/mg) *by* **7** *and* **8**. The IC_{50} was determined at 30° using a 0.073M NaOAc/HCl buffer (pH 4.5) and 4-nitrophenyl *β*-D-glucuronide·H_2O (*Fluka*) as substrate.

Measurements were started by addition of a 10 mM soln. of the substrate (50 µl) to the mixed solns. of the buffer (800 µl), the enzyme (50 µl, *ca.* 0.04 U), **7** (200 µl; 6.38, 3.2, 1.60, 0.32 and 0 µmol), and **8** (200 µl; 21.79, 12.30, 10.90, 6.15, 2.83 and 0 mmol), resp. The hydrolyses were quenched by the addition of a soln. of NaOH (0.5M, 2 ml) after 1, 3 and 5 min (**7**), and 1, 2 and 3 min (**8**), resp. The increase of absorption per minute at 405 nm was taken as the velocity for the hydrolysis of the substrate. This increase was linear during all measurements.

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