Carbohydrate Research, 217 (1991) 59–70
Elsevier Science Publishers B.V., Amsterdam

Synthesis of four diastereomeric octofuranoses from D-glucofuranurono-6,3-lactone *via* Grignard reactions

Karl Dax, Martin Fechter, Günther Gradnig, Vera Grassberger, Carina Illaszewicz, Markus Ungerank, and Arnold E. Stütz
Institut für Organische Chemie, Technische Universität Graz, Stremayrgasse 16, A-8010 Graz (Austria)

(Received August 27th, 1990; accepted in revised form October 29th, 1990)

ABSTRACT

Reduction of 5-*O*-*tert*-butyldimethylsilyl-1,2-*O*-isopropylidene-α-D-gluco- (**2**) and -β-L-idofuranurono-6,3-lactone (**3**) with diisobutylaluminum hydride (DIBAL-H) to the respective hemiacetal at C-6, followed by reaction with vinylmagnesium bromide in either ether or tetrahydrofuran, gives the corresponding diastereomeric pairs of 7,8-dideoxyoct-7-eno-1,4-furanoses. The configurations of the products at C-6 were determined after oxidative cleavage of the terminal double bond and reduction of the aldehyde by conversion of the resulting heptoses into the known corresponding per-*O*-acetylated heptitols.

INTRODUCTION

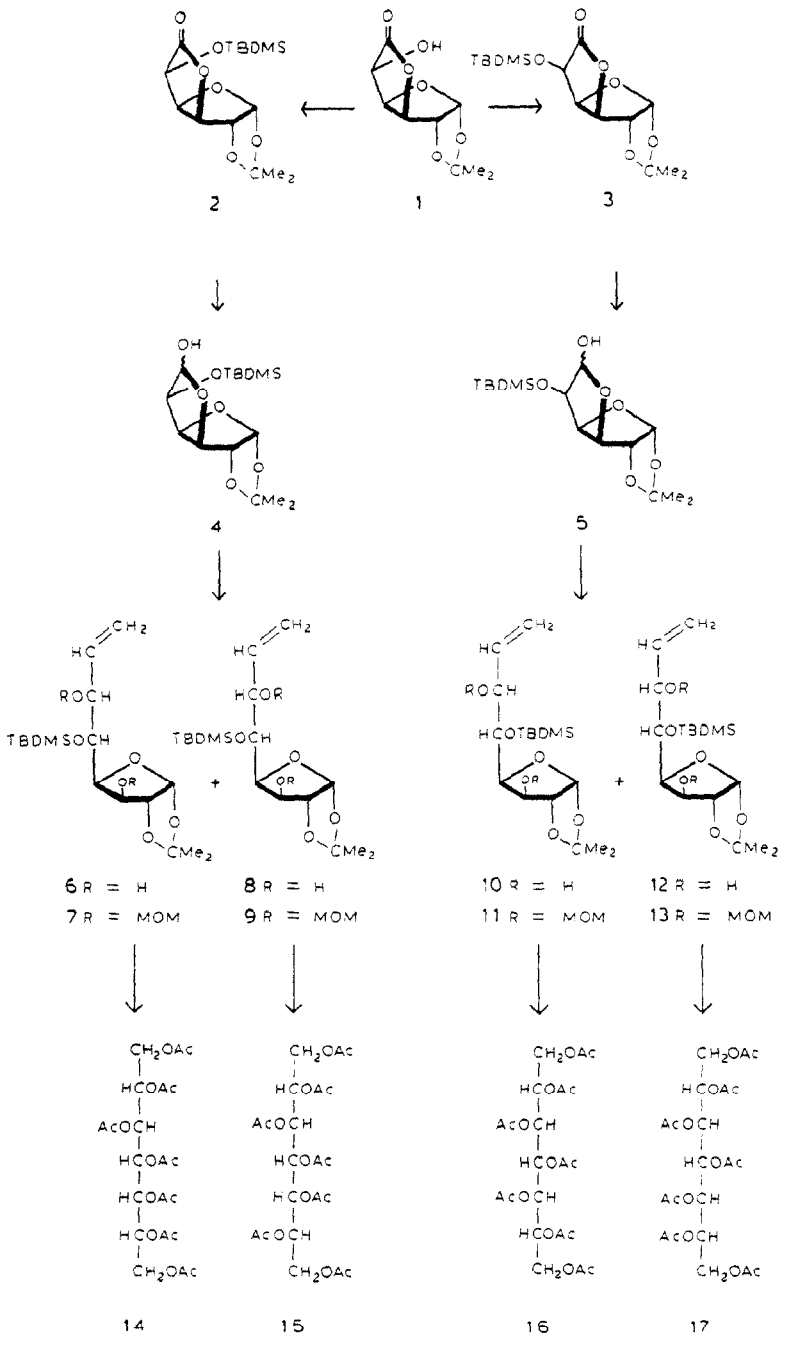
Higher carbon sugars have attracted considerable interest as constituents of various antibiotics[1], *e.g.*, hikizimycin[2] or tunicamycins[3], other natural products such as Kdo[4] and sialic acids[5], intermediates in several syntheses of biologically active compounds[6,7] and as precursors of *C*-glycosyl compounds[8,9,10]. In their own right, they have served, for example, as probes to determine scope and limitations of modern synthetic chain-extension and functionalization techniques[11,12].

Chain-extension at the reducing[8,13,14] or non-reducing[6,11,15] end of suitably protected derivatives of hexopyranoses and pentofuranoses have been investigated. Only a little information[12], however, has been available on methodology and especially on the stereochemical outcome of chain-elongation reactions at C-6 of suitable derivatives of hexofuranoses. In connection with our continued interest[16] in the stereochemical problems related to synthetic applications of D-glucofuranurono-6,3-lactone and its derivatives, we investigated the reaction of 5-*O*-*tert*-butyldimethylsilyl-1,2-*O*-isopropylidene-α-D-*gluco*- (**4**) and -β-L-*ido*-hexodialdodifuranose (**5**) with vinylmagnesium bromide.

RESULTS AND DISCUSSION

Reduction of 5-*O*-*tert*-butyldimethylsilyl-1,2-*O*-isopropylidene-α-D-glucofuranurono-6,3-lactone (**2**) (ref. 17), which was synthesized by an improved procedure not requiring chromatographic purification, with diisobutylaluminum hydride (DIBAL-H)

0008-6215/91/$ 03.50



TBDMS, *tert*-butyldimethylsilyl; MOM, methoxymethyl

Scheme 1.

at −30° gave hexodialdose **4** in over 90% yield. Reaction of **4** with vinylmagnesium bromide in tetrahydrofuran at −35° furnished an inseparable 1:1 mixture of the respective oct-7-enofuranoses **6** and **8** in 94% yield. This mixture was treated with chloromethyl methyl ether in dry dichloromethane in the presence of *N*-ethyldiisopropyl amine at ambient temperature for 24 h to give the respective 3,6-di-*O*-methoxymethyl derivatives **7** and **9**, which could easily be separated by chromatography. In contrast to the outcome of attempted benzylation reactions with benzyl bromide in tetrahydrofuran–*N*,*N*-dimethylformamide in the presence of sodium hydride which led to O-6-silylated products, no migration of the silyl group occurred under these conditions, as was shown by the chemical shift of H-5 after desilylation and acetylation of O-5 (ref. 18).

In order to obtain additional information on the parameters influencing the stereochemical outcome of this Grignard reaction, as well as to address the potential problem of epimerization at C-5, a side reaction which can occur even under mildly basic conditions[19], the chain-extension was also performed with the L-*ido*-epimer of **2**.

5-*O*-*tert*-Butyldimethylsilyl-1,2-*O*-isopropylidene-β-L-idofuranurono-6,3-lactone (**3**), which is readily available from 1,2-*O*-isopropylidene-α-D-glucofuranurono-6,3-lactone (**1**) using Klemer's method[20] *via* 1,2-*O*-isopropylidene-β-L-idofuranurono-6,3-lactone[21] in three steps and 65% overall yield, was reduced with DIBAL-H in dichloromethane at −30° to yield the corresponding hexodialdofuranose **5**. In contrast to the remarkably poor stereoselection with the D-*gluco* epimer **4**, L-*ido*-dialdose **5** reacted with vinylmagnesium bromide to give a 10:1 mixture of the respective diastereomeric 7-eno-sugars **10** and **12**, which could be resolved chromatographically. The pure products were transformed into the corresponding 3,6-di-*O*-methoxymethyl derivatives **11** and **13**, both of which were different from the compounds obtained in the D-*gluco*-series. Epimerization at C-5 during the reduction or in the chain-extension step could therefore be excluded. The n.m.r. spectroscopic data of the protected 7-eno-sugars obtained did not allow unambiguous assignments of their configurations at C-6, so we decided to resort to additional chemical means for the elucidation of their structure.

In order to firmly establish the configurations of compounds **7**, **9**, **11**, and **13** at C-6, we chose the approach as follows: The chromatographically more mobile product in the D-*gluco* series, **7**, was chemically degraded by consecutive treatment with (*i*) osmium tetroxide–sodium metaperiodate in 1:1 water–ether, (*ii*) with sodium borohydride in methanol, followed by (*iii*) reaction with aq. trifluoroacetic acid (10%) to remove the protecting groups. Reduction of the free heptose with sodium borohydride in methanol and conventional acetylation of the crude heptitol yielded a crystalline product whose ^{1}H- and ^{13}C-n.m.r. spectra were identical with those of hepta-*O*-acetyl-D-*glycero*-D-*gluco*-heptitol **14** (ref. 22). This result firmly established the stereochemical relationship of O-5 and O-6 to be *erythro* in compound **7** and thus proves the structure depicted in the scheme.

Analogously the same sequence of reactions applied to the chromatographically less mobile isomer **9** gave the hepta-*O*-acetyl derivative of L-*glycero*-D-*galacto*-heptitol (**15**), which gave the same n.m.r. spectroscopic features as its enantiomer[22]. Thus **9** is proven to be an L-*glycero*-D-*gluco*-oct-7-enose derivative.

TABLE I

300 MHz ^{1}H-n.m.r. data for compounds in $CDCl_3$

Compound	*Chemical shifts* (δ)									
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-7*	*H-8*	*H-8'*	*Others*[a]
2	6.00	4.76	4.72	4.80	4.51	—	—	—	—	1.50, 1.32 (Me_2C); 0.93, 0.19, 0.15 (TBDMS)
3	5.89	4.80	5.00	4.59	4.20	—	—	—	—	1.52, 1.34 (Me_2C); 0.89, 0.17, 0.15 (TBDMS)
7	5.83	4.79	4.03	3.92	4.17	4.23	5.83	5.34	5.29	4.82–4.55, 3.40, 3.36 (2 MOM); 1.44, 1.31 (Me_2C); 0.88, 0.14, 0.05 (TBDMS)
9	5.87	4.77	4.06	4.22	4.08	4.24	5.91	5.31	5.28	4.78–4.59, 3.38, 3.36 (2 MOM); 1.44, 1.28 (Me_2C); 0.87, 0.10, 0.02 (TBDMS)
10	6.08	4.65	4.36	4.18	4.22	4.53	6.11	5.50	5.39	1.63, 1.47 (Me_2C); 1.06, 0.29, 0.25 (TBDMS)
11	5.89	4.79	3.96	3.90	4.12	4.01	5.95	5.35	5.27	4.80–4.59, 3.42, 3.37 (2 MOM); 1.45, 1.30 (Me_2C); 0.90, 0.10, 0.08 (TBDMS)
12	5.92	4.47	4.22	3.94	4.02	4.22	5.96	5.33	5.22	1.45, 1.30 (Me_2C); 0.88, 0.14, 0.11 (TBDMS) 3.15, 3.83 (2 OH).
13	5.90	4.60	3.96	3.90	4.13	3.97	5.96	5.33	5.26	4.74–4.51, 3.43, 3.33 (2 MOM); 1.45, 1.30 (Me_2C); 0.91, 0.12, 0.09 (TBDMS)
18	5.86	4.79	4.05	4.00	4.17	3.70	1.54		0.96	4.80–4.55, 3.37, 3.36 (2 MOM); 1.45, 1.28 (Me_2C); 0.85, 0.09, −0.02 (TBDMS)
19	5.84	4.71	4.11	4.04	4.11	3.52	1.65		0.93	4.77–4.63, 3.36, 3.35 (2 MOM); 1.44, 1.27 (Me_2C); 0.85, 0.09, 0.03 (TBDMS)
20	5.92	4.61	4.18	4.30	4.01	3.49	1.72		0.91	4.72–4.63, 3.40, 3.39 (2 MOM); 1.47, 1.31 (Me_2C); 0.90, 0.15, 0.11 (TBDMS)
21	5.87	4.62	3.88	3.96	4.08	3.42	1.69		0.98	4.72–4.49, 3.40, 3.36 (2 MOM); 1.46, 1.29 (Me_2C); 0.89, 0.08, 0.06 (TBDMS)

Compound	*Coupling constants (Hz)*[b]						
	$J_{1,2}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	$J_{7,8}$	$J_{7,8'}$
$J_{8,8'}$							
2	3.7	3.0	4.1	—	—	—	—
—							
3	3.6	2.9	—	—	—	—	—
—							
7	3.5	2.6	9.3	1.8	8.6	15.4	10.4
1.9							
9	3.5	2.7	8.8	1.9	5.8	17.8	10.3
1.5							
10	3.7	1.8	6.9	1.5	4.5	17.2	10.6
< 1							
11	3.9	2.9	8.7	2.3	8.7	17.6	10.3
1.6							
12	3.6	< 1	6.6	2.4	< 1	17.2	10.5
< 1							
13	3.7	2.8	8.6	2.4	8.7	17.4	10.3
1.7							
18	3.6	2.6	9.0	1.2	8.6	7.4	—
—							
19	3.6	< 1	< 1	< 1	7.1	7.4	—
—							
20	3.8	3.0	8.0	2.0	7.0	7.4	—
—							
21	3.5	2.6	8.2	1.9	[c]	7.4	—
—							

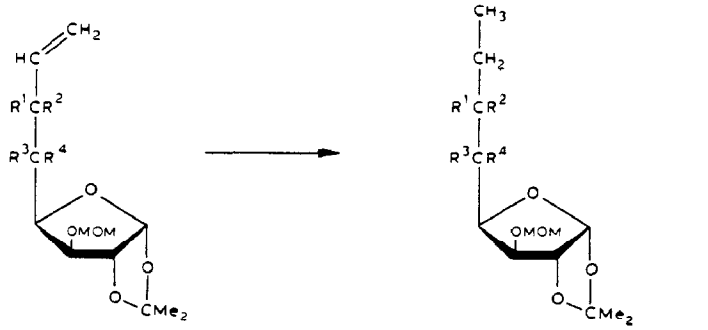
[a] Abbreviations include TBDMS, *tert*-butyldimethylsilyl, and MOM, methoxymethyl. [b] $J_{2,3}$ < 0.5 Hz. [c] Not resolved.

TABLE II

^{13}C-N.m.r. chemical shifts for compounds in $CDCl_3$

Compound	*Chemical shifts* (δ)								
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*Others*[a]
2	107.1		82.9, 81.5, 79.1		71.8	173.2	—	—	113.1, 27.1, 26.7 (Me_2C); 25.9, 18.7, −4.6, −5.0 (TBDMS)
3	106.5		84.6, 83.5, 82.2		72.6	173.6	—	—	113.2, 27.2, 26.7 (Me_2C); 25.8, 18.4, −4.8, −5.0 (TBDMS)
7	105.1	82.8	82.8	80.4	71.5	79.3	134.0	120.0	112.1, 27.1, 26.9 (Me_2C); 26.4, 18.7, −3.2, −3.8 (TBDMS); 98.2, 93.9, 56.1, 55.8 (2 MOM)
9	104.9	82.8	82.0	79.6	72.4	78.4	136.1	118.8	111.7, 26.9, 26.6 (Me_2C); 26.3, 18.7, −3.3, −3.8 (TBDMS); 97.4, 94.4, 56.0, 55.8 (2 MOM)
10	104.5	85.3	82.2	73.9[b]	73.4[b]	71.5[b]	138.0	115.6	111.6, 27.0, 26.5 (Me_2C); 24.3, 18.4, −4.2, −4.6 (TBDMS)
11	104.4	83.6	81.7	81.2	73.4	78.6	134.6	120.1	111.7, 27.0, 26.7 (Me_2C); 26.2, 18.8, −4.2, −4.4 (TBDMS); 97.0, 93.3, 56.6, 56.0 (2 MOM)
12	104.6	85.2	82.8	75.5[b]	75.0[b]	74.7[b]	137.9	117.2	111.8, 27.0, 26.6 (Me_2C); 26.2, 18.6, −3.9, −4.3 (TBDMS)
13	104.2	83.6	81.7	81.4	73.5	77.7	134.6	120.0	111.7, 27.0, 26.7 (Me_2C); 26.2, 18.8, −4.2, −4.4 (TBDMS); 97.0, 93.2, 56.6, 55.5 (2 MOM)
18	105.0	82.8	82.8	80.2	70.4	77.7	21.6	11.1	111.9, 27.1, 26.7 (Me_2C); 26.3, 18.8, −3.9, −4.1 (TBDMS); 98.0, 95.8, 56.1, 56.0 (2 MOM)
19	105.2	82.7	82.3	81.4	69.9	79.8	23.4	11.1	111.8, 27.0, 26.8 (Me_2C); 26.3, 18.7, −3.3, −3.7 (TBDMS); 97.6, 97.1, 56.1, 55.8 (2 MOM)
20	104.6	83.8[b]	81.7[b]	81.3[c]	71.5	80.3[c]	23.2	10.8	111.8, 27.0, 26.8 (Me_2C); 26.4, 18.8, −3.5, −4.6 (TBDMS); 97.3, 96.1, 56.5, 56.1 (2 MOM)
21	104.3	83.6	81.8	81.8	72.3	78.5	22.7	11.0	111.6, 27.0, 26.6 (Me_2C); 26.2, 18.7, −4.2, −4.8 (TBDMS); 97.5, 94.7, 56.5, 55.8 (2 MOM)

[a] Abbreviations include TBDMS, *tert*-butyldimethylsilyl, and MOM, methoxymethyl. [b,c] Assignments with the same indices in one line can be interchanged.



7 R^1 = OMOM R^2 = H R^3 = OTBDMS R^4 = H

9 R^1 = H R^2 = OMOM R^3 = OTBDMS R^4 = H

11 R^1 = OMOM R^2 = H R^3 = H R^4 = OTBDMS

13 R^1 = H R^2 = OMOM R^3 = H R^4 = OTBDMS

18 R^1 = OMOM R^2 = H R^3 = OTBDMS R^4 = H

19 R^1 = H R^2 = OMOM R^3 = OTBDMS R^4 = H

20 R^1 = OMOM R^2 = H R^3 = H R^4 = OTBDMS

21 R^1 = H R^2 = OMOM R^3 = H R^4 = OTBDMS

Scheme 2

In the L-*ido*-series the chromatographically less polar main product **13** gave hepta-*O*-acetyl-L-*glycero*-L-*gulo*-heptitol (**17**), while the less-mobile side product **11** could be degraded to hepta-*O*-acetyl-*glycero*-*ido*-heptitol (**16**), which exhibited very simple ^{1}H- and ^{13}C-n.m.r. spectra by virtue of its *meso*-configuration[22].

The protected diastereomeric 7,8-dideoxyoct-7-enofuranoses, epimeric at C-5 and/or C-6 are deemed to be interesting intermediates for various syntheses due to the selective availability of O-5 and C-5, respectively, upon treatment with tetrabutylammonium fluoride. The synthetic potential of the terminal double bond gives access, for example, to further chain extension, as well as functionalization of the chain.

Hydrogenation of the double bond in enofuranoses **7**, **9**, **11**, and **13** over palladium-on-carbon led to the corresponding fully protected saturated 7,8-dideoxyoctofuranoses **18**, **19**, **20**, and **21**, respectively (Scheme 2). These were needed for the structure determination of 7-deoxy-octofuranoses obtained by a different approach to chain-extended sugars.

EXPERIMENTAL

General methods. — Melting points were recorded on a Tottoli apparatus and are uncorrected. Optical rotations were measured of 1–5% solutions in chloroform on a JASCO digital polarimeter with a path length of 10 cm. ^{1}H-N.m.r. spectra (at 300 MHz) and ^{13}C-n.m.r. spectra (at 75 MHz) were recorded on a Bruker MSL 300 spectrometer. Signals in the ^{13}C-n.m.r. spectra were assigned by ^{1}H–^{13}C heteronuclear shift-correlation experiments. In cases where necessary, the assignments of proton signals were con-

firmed by ^1H–^1H homonuclear shift-correlation experiments. T.l.c. was performed on precoated aluminum sheets (E. Merck 5554) using petroleum ether–ethyl acetate mixtures as solvent systems (petroleum ether–ethyl acetate 2:1, 1:1, or 1:2 v/v, respectively, for protected compounds). Zones were visualized by spraying with a solution of vanillin (5% w/v) in conc. sulfuric acid and warming. For column chromatography Silica Gel 60 (E. Merck) was used. Dry solvents were used for all reactions.

General procedure for O-*silylations.* — To a 10% solution (w/v) of the respective lactone in dry *N,N*-dimethylformamide, imidazole (3 equiv.) and *tert*-butyldimethylchlorosilane (1.5 equiv.) were added, and the mixture was kept at ambient temperature until all starting material had reacted. Dichloromethane (200 mL) was then added, the solution was washed with 5% aq. HCl and 5% aq. sodium hydrogencarbonate, dried (sodium sulfate), and the solvent was evaporated under reduced pressure. The crude product was crystallized from ethyl acetate–petroleum ether.

General procedure for DIBAL-H reductions. — To a 10% solution (w/v) of the respective silylated lactone in dry dichloromethane, DIBAL-H (1.3 equiv.) was added as a M solution in toluene at $-30°$. The progress of the reaction was monitored by t.l.c. Subsequent extraction with 5% aq. HCl and 5% aq. sodium hydrogencarbonate, drying (sodium sulfate) of the organic layer, and evaporation of the solvent under reduced pressure furnished a white crystalline material which was pure enough for use in the next step. To obtain analytical samples, the products were recrystallized from ethyl acetate–petroleum ether.

General procedure for reactions with vinylmagnesium bromide. — To a M solution of 3 equiv. of vinylmagnesium bromide (Aldrich, 22,558-4) in tetrahydrofuran, a 10% solution (w/v) of the respective lactol in the same solvent was added at $-10°$, and the mixture was stirred until all starting material was consumed. Dichloromethane was added, and the organic layer was consecutively washed with 5% aq. HCl and aq. sodium hydrogencarbonate. It was dried (sodium sulfate), and the solvent was removed *in vacuo*. The crude products were chromatographically purified (petroleum ether–ethyl acetate 10:1, v/v).

General procedure for O-*methoxymethylations.* — To a 10% solution (w/v) of the respective 3,6-diol in dry dichloromethane, chloromethyl methyl ether (3 equiv.) and *N*-ethyldiisopropyl amine (4 equiv.) were added, and the mixture was stirred at 40° until no remaining starting material could be detected by t.l.c. After subsequent extraction with 5% aq. HCl and 5% aq. sodium hydrogencarbonate, the organic layer was dried (sodium sulfate), and the solvent was removed under reduced pressure. The crude products were purified chromatographically (petroleum ether–ethyl acetate 10:1, v/v).

General procedure for the oxidative cleavage of the terminal double bond. — To a satd. aq. solution of sodium metaperiodate (50 mL), a 5% solution (w/v) of the respective olefin in diethyl ether and a catalytic amount of osmium tetroxide were added, and the resulting heterogeneous mixture was vigorously stirred at ambient temperature until all starting material was converted to a chromatographically less mobile product. The organic layer was separated, dried (sodium sulfate), and concen-

trated under reduced pressure. The resulting yellow syrup was immediately used in the next step.

General procedure for sodium borohydride reductions. — To a solution of sodium borohydride (10 equiv.) in ice-cold methanol, a 20% solution (w/v) of the respective aldehyde or hemiacetal in the same solvent was added dropwise. After the gas evolution had ceased, ethyl acetate was added to decompose excess reducing agent. In the case of the protected heptoses, dichloromethane was added, and the mixture was consecutively washed with 5% aq. HCl and aq. sodium hydrogencarbonate. After drying the organic layer with sodium sulfate, the solvent was removed under reduced pressure, and the resulting crude product was taken directly to the next step.

In the case of the deprotected heptoses, the reaction mixture was neutralized with Amberlite IR-120 [H^+] and concentrated twice from methanol. The crude residue was taken directly to the next step.

General deprotection procedure. — To a sample of the respective, partially protected heptofuranose (150–300 mg), 10% aq. trifluoroacetic acid (20 mL) was added, and the mixture was stirred for 48 h at 40°. The clear solution was neutralized with basic ion-exchange resin (Merck III) and concentrated. The resulting crude, deprotected heptose was taken directly to the next step.

General O-*acetylation procedure.* — To a 10% solution of the crude, respective heptitol in dry pyridine, acetic anhydride (ca. 30 equiv.) and *N,N*-dimethylaminopyridine (~ 10 mol%) were added, and the mixture was kept at ambient temperature for 24 h. Methanol was added, and after a further 20 min the mixture was concentrated under reduced pressure. The residue was partitioned between dichloromethane (20 mL) and 5% aq. HCl, and the organic layer was washed with 5% aq. sodium hydrogencarbonate (20 mL). The organic phase was dried (sodium sulfate), and the solvent was removed under reduced pressure. The respective peracetylated heptitol was purified by chromatography (petroleum ether–ethyl acetate 3:1, v/v).

General hydrogenation procedure. — A solution of the respective fully protected oct-7-enofuranose (200 mg, 0.45 mmol) in methanol (15 mL) was shaken with palladium-on-charcoal (5%, 30 mg) under an atmosphere of hydrogen (2 bar) for 6 h. The catalyst was filtered off, the solvent was removed under reduced pressure, and the residual colourless syrup was purified on silica gel (petroleum ether–ethyl acetate 10:1, v/v) to give the respective saturated 7,8-dideoxy-octofuranose.

*5-*O*-tert-Butyldimethylsilyl-1,2-*O*-isopropylidene-α-*D*-glucofuranurono-6,3-lactone* (**2**). — 1,2-*O*-Isopropylidene-α-D-glucofuranurono-6,3-lactone[20] (10.0 g, 46.3 mmol) was reacted according to the general *O*-silylation procedure to give **2**[17] (14.7 g, 96%), $[\alpha]_D^{20}$ +50°, m.p. 114–116°. Lit.[17] $[\alpha]_D^{20}$ +44.2° (dioxane), m.p. 118–119°.

*5-*O*-tert-Butyldimethylsilyl-1,2-*O*-isopropylidene-α-*D*-gluco-hexodialdodifuranose* (**4**). —Compound **2** (10.0 g, 30.3 mmol) was subjected to the general procedure for DIBAL-H reductions to give **4** (9.50 g, 94%), $[\alpha]_D^{20}$ +40.6°, as a syrup.

Anal. Calc. for $C_{15}H_{28}O_6Si$: C, 54.19; H, 8.49. Found: C, 54.12; H, 8.53.

*5-*O*-tert-Butyldimethylsilyl-7,8-dideoxy-1,2-*O*-isopropylidene-3,6-di-*O*-methoxymethyl-α-*D*-glycero-*D*-gluco-hept-7-enofuranose* (**7**) and *5-*O*-tert-butyldimethylsilyl-7,8-*

dideoxy-1,2-O-isopropylidene-3,6-di-O-methoxymethyl-β-L-glycero-D-gluco-hept-7-enofuranose (**9**). — Application of the general procedure for reactions with vinylmagnesium bromide to **4** (5.0 g, 15.0 mmol) gave 5.10 g (94%) of a diastereomeric mixture of **6** and **8**. As these products were not separable at this stage, the mixture was subjected to the general methoxymethylation procedure. The chromatographically more mobile epimer **7** (3.05 g, 48%) was obtained as a colourless syrup, $[\alpha]_D^{20}$ −22.0°

Anal. Calc. for $C_{21}H_{40}O_8Si$: C, 56.22; H, 8.99. Found: C, 56.31; H, 9.09.

The chromatographically less mobile isomer **9** (2.92 g, 46%) was also isolated as a syrup, $[\alpha]_D^{20}$ +30.0°.

Anal. Calc. for $C_{21}H_{40}O_8Si$: C, 56.22; H, 8.99. Found: C, 56.16; H, 8.91.

5-O-tert-Butyldimethylsilyl-1,2-O-isopropylidene-β-L-idofuranurono-6,3-lactone (**3**). — Following the general procedure for *O*-silylation, 1,2-*O*-isopropylidene-β-L-idofuranurono-6,3-lactone[21] (10.0 g, 46.3 mmol) gave **3** (13.9 g, 91%) as white crystals, $[\alpha]_D^{20}$ +68.5°, m.p. 58°.

Anal. Calc. for $C_{15}H_{26}O_6Si$: C, 54.52; H, 7.93. Found: C, 54.39; H, 8.02.

5-O-tert-Butyldimethylsilyl-1,2-O-isopropylidene-β-L-ido-hexodialdodifuranose (**5**). — The general procedure for reductions with DIBAL-H applied to **3** (6.0 g, 18.2 mmol) gave crystalline **5** (6.55 g, 92%), $[\alpha]_D^{20}$ −7.1°, m.p. 75–78°.

Anal. Calc. for $C_{15}H_{28}O_6Si$: C, 54.19; H, 8.49. Found: C, 54.22, H, 8.56.

5-O-tert-Butyldimethylsilyl-7,8-dideoxy-1,2-O-isopropylidene-α-D-glycero-L-ido-hept-7-enofuranose (**10**) and *5-O-tert-butyldimethylsilyl-7,8-dideoxy-1,2-O-isopropylidene-β-L-glycero-L-ido-hept-7-enofuranose* (**12**). — Subjecting **5** (5.0 g, 15.0 mmol) to the general procedure for reactions with vinylmagnesium bromide furnished as the main product **12** (4.0 g, 74%) as a colourless syrup, $[\alpha]_D^{20}$ −24.4°.

Anal. Calc. for $C_{17}H_{32}O_6Si$: C, 56.64; H, 8.95. Found: C, 56.50; H, 9.04.

Syrupy **10** (410 mg, 7.5%) was isolated as a byproduct, $[\alpha]_D^{20}$ +3.2°.

Anal. Calc. for $C_{17}H_{32}O_6Si$: C, 56.64; H, 8.95. Found: C, 56.74; H, 9.02.

5-O-tert-Butyldimethylsilyl-7,8-dideoxy-1,2-O-isopropylidene-3,6-di-O-methoxymethyl-α-D-glycero-L-ido-hept-7-enofuranose (**11**). — Processing of **10** (400 mg, 1.11 mmol) according to the general procedure for methoxymethylations led to syrupy **11** (410 mg, 82%), $[\alpha]_D^{20}$ +30.7°.

Anal. Calc. for $C_{21}H_{40}O_8Si$: C, 56.22; H, 8.99. Found: C, 56.35; H, 9.07.

5-O-tert-Butyldimethylsilyl-7,8-dideoxy-1,2-O-isopropylidene-3,6-di-O-methoxymethyl-β-L-glycero-L-ido-hept-7-enofuranose (**13**). — Following the general procedure for methoxymethylations, **12** (3.50 g, 9.7 mmol) gave **13** (3.70 g, 85%) as a syrup, $[\alpha]_D^{20}$ +31.9°.

Anal. Calc. for $C_{21}H_{40}O_8Si$: C, 56.22; H, 8.99. Found: C, 56.11; H, 9.07.

Hepta-O-acetyl-D-glycero-D-gluco-heptitol (**14**), *hepta-O-acetyl-L-glycero-D-galacto-heptitol* (**15**), *hepta-O-acetyl-meso-glycero-ido-heptitol* (**16**) and *hepta-O-acetyl-L-glycero-L-gulo-heptitol* (**17**). — Individual sequential application of the general procedure for the oxidative degradation of the terminal double bond, the general procedure for sodium borohydride reductions, the general deprotection procedure and, again, the general procedure for sodium borohydride reductions, followed by the general acetyla-

tion procedure to samples (150–300 mg each) of the fully protected oct-7-enofuranoses **7**, **9**, **11**, and **13**, respectively, gave analytical samples of the corresponding peracetylated heptitols **14**, **15**, **16**, and **17**, respectively. The ^{1}H- and ^{13}C-n.m.r. spectra of these compounds have been reported[22].

5-O-tert-*Butyldimethylsilyl-7,8-dideoxy-1,2*-O-*isopropylidene-3,6-di*-O-*methoxymethyl*-α-D-glycero-D-gluco-*octofuranose* (**18**). — Hydrogenation of enofuranose **7** following the general procedure yielded **18** (180 mg, 90%) as a colourless syrup, $[\alpha]_D^{20}$ +55.6°.

Anal. Calc. for $C_{21}H_{42}O_8Si$: C, 55.97; H, 9.39. Found: C, 55.91; H, 9.42.

5-O-tert-*Butyldimethylsilyl-7,8-dideoxy-1,2*-O-*isopropylidene-3,6-di*-O-*methoxymethyl*-β-L-glycero-D-gluco-*octofuranose* (**19**). — Applying the general hydrogenation procedure to enofuranose **9** gave syrupy **19** (175 mg, 87%), $[\alpha]_D^{20}$ −9.8°.

Anal. Calc. for $C_{21}H_{42}O_8Si$: C, 55.97; H, 9.39. Found: C, 55.87; H, 9.44.

5-O-tert-*Butyldimethylsilyl-7,8-dideoxy-1,2*-O-*isopropylidene-3,6-di*-O-*methoxymethyl*-α-D-glycero-L-ido-*octofuranose* (**20**). — According to the general procedure enofuranose **11** was hydrogenated to give **20** (175 mg, 87%) as a pale yellow syrup, $[\alpha]_D^{20}$ −23.6°.

Anal. Calc. for $C_{21}H_{42}O_8Si$: C, 55.97; H, 9.39. Found: C, 56.00; H, 9.45.

5-O-tert-*Butyldimethylsilyl-7,8-dideoxy-1,2*-O-*isopropylidene-3,6-di*-O-*methoxymethyl*-β-L-glycero-L-ido-*octofuranose* (**21**). — Subjecting enofuranose **13** to the general hydrogenation procedure furnished syrupy **21** (170 mg, 85%), $[\alpha]_D^{20}$ −42.1°.

Anal. Calc. for $C_{21}H_{42}O_8Si$: C, 55.97; H, 9.39. Found: C, 55.92; H, 9.48.

ACKNOWLEDGMENTS

We thank Dipl.-Ing. H. Baumgartner and Dipl.-Ing. H.-J. Weber for recording some of the n.m.r. spectra, and we appreciate the financial support from *Fonds zur Förderung der wissenschaftlichen Forschung. Vienna* (project 7335).

REFERENCES

1 P. M. Collins (Ed.), *Carbohydrates*, Chapman and Hall Chemistry Sourcebooks, Chapman and Hall, London, 1987.
2 M. Vuilhorgne, S. Ennifar, B. C. Das, J. W. Paschal, R. Nagarajan, E. W. Hagaman, and E. Wenkert, *J. Org. Chem.*, 42 (1977) 3289–3291.
3 K. Eckhardt, W. Ihn, D. Tresselt, and D. Krebs, *J. Antibiot.*, 34 (1981) 1631–1632.
4 F. M. Unger, *Adv. Carbohydr. Chem. Biochem.*, 38 (1981) 323–388.
5 R. Schauer, *Adv. Carbohydr. Chem. Biochem.*, 40 (1982) 132–234.
6 J. A. Secrist III and K. D. Barnes, *J. Org. Chem.*, 45 (1980) 4526–4528.
7 S. J. Danishefsky, E. Larson, and J. P. Springer, *J. Am. Chem. Soc.*, 107 (1985) 1274–1280.
8 A. Boschetti, F. Nicotra, L. Panza, and G. Russo, *J. Org. Chem.*, 53 (1988) 4181–4185.
9 M. D. Lewis, J. K. Cha, and Y. Kishi, *J. Am. Chem. Soc.*, 104 (1982) 4976–4978.
10 S. Jarosz, D. Mootoo, and B. Fraser-Reid, *Carbohydr. Res.*, 147 (1986) 59–68.
11 J. K. Cha, W. J. Christ, and Y. Kishi, *Tetrahedron*, 40 (1984) 2247–2255.
12 J. C. Barnes, J. S. Brimacombe, and G. McDonald, *J. Chem. Soc., Perkin Trans. 1*, (1989) 1483–1489 and refs. cited therein.
13 D. Horton and W. Priebe, *Carbohydr. Res.*, 94 (1981) 27–41 and refs. cited therein.

14 V. K. Srivastava and L. M. Lerner, *J. Org. Chem.*, 44 (1979) 3368–3373.
15 S. Czernecki and J.-M. Valery, *J. Carbohydr. Chem.*, 7 (1988) 151–156 and refs. cited therein.
16 R. Albert, K. Dax, A. E. Stütz, H. Zekoll, and H. Sterk, *J. Carbohydr. Chem.*, 7 (1988) 537–554; K. Dax, B. Gaigg, V. Grassberger, B. Kölblinger, and A. E. Stütz, *J. Carbohydr. Chem.*, 9 (1990) 479–500.
17 H. P. Wessel, *J. Carbohydr. Chem.*, 8 (1989) 443–455.
18 M. Fechter, V. Grassberger, M. Ungerank, and A. E. Stütz, unpublished results.
19 K. Dax, A. P. Rauter, A. E. Stütz, and H. Weidmann, *Justus Liebigs Ann. Chem.*, (1981) 1768–1773.
20 A. Klemer, U. Hofmeister, and R. Lemmes, *Carbohydr. Res.*, 68 (1979) 391–395.
21 R. Csuk, H. Hönig, J. Nimpf, and H. Weidmann, *Tetrahedron Lett.*, 21 (1980) 2135–2136.
22 S. J. Angyal and R. Le Fur, *Carbohydr. Res.*, 126 (1984) 15–26; S. J. Angyal, J. K. Saunders, C. T. Grainger, R. Le Fur, and P. G. Williams, *Carbohydr. Res.*, 150 (1986) 7–21.