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Radical cyclisation of hept-1-enitols*

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ABSTRACT

7-Deoxy-7-iodohept-1-enitols react intramolecularly to give 5-carba analogues of pyranoses (pseudo sugars) by the action of tributyltin hydride, which generates a radical at C-7. The configuration at the new chiral centre depends on the relative orientation of the oxygen functions in the starting material and the pattern of substitution.

INTRODUCTION

The 5a-carbapyranoses ("pseudo sugars"[1]) have interesting biological properties[2]. Our interest in this class of compound relates to their potential for the synthesis of natural products.

Most of the known syntheses of 5-carba sugars are costly and we have sought simpler routes. We now report on one such reaction that involves the cyclisation of hept-1-enitols, in which a radical is generated at an appropriate distance from the double bond.

RESULTS

Synthesis of the starting materials. — Acyclic carbohydrate derivatives with the *allo* and *ido* configurations should be most amenable to intramolecular cyclisation reactions because the two 1,3-type interactions that occur in the planar zigzag conformation of these molecules give rise to two sickle elements that favour the formation of cylic products[3]. The D-*allo*-hept-1-enitol derivative **3** is available readily (79%) by chain elongation of the 5-*O*-*tert*-butyldimethylsilyl derivative (**2**) of 2,3-*O*-isopropylidene-D-ribofuranose (**1**) via a Grignard-type reaction[4] with vinylmagnesium bromide.

The *allo* configuration of **3** was established by its conversion into the known[4] trityl derivative **4**. Benzylation of **3** gave **5**, desilylation of which gives **6**. Because bromides are good precursors of radicals[5], **6** was transformed first into the 7-bromo-7-deoxy deriv-

* 5-Carba Analogues of Sugars, Part I. This work was carried out at the Institut für Organische Chemie der Universität Hamburg.
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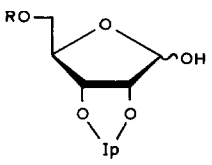
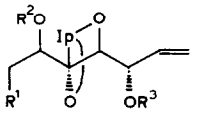
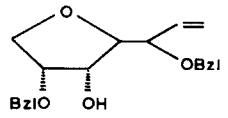


1 R = H
2 R = ^{t}BuMe$_2$Si



3 R^1 = ^{t}BuMe$_2$SiO, R^2 = R^3 = H
4 R^1 = TrO , R^2 = R^3 = H
5 R^1 = ^{t}BuMe$_2$SiO , R^2 = R^3 = Bzl
6 R^1 = OH , R^2 = R^3 = Bzl
7 R^1 = Br , R^2 = R^3 = Bzl
9 R^1 = I , R^2 = R^3 = Bzl
12 R^1 = OH , R^2 = R^3 = H
13 R^1 = OTs , R^2 = R^3 = H
14 R^1 = I , R^2 = R^3 = H
15 R^1 = I , R^2 = R^3 = Ac
16 R^1 = I , R^2 = R^3 = Bz



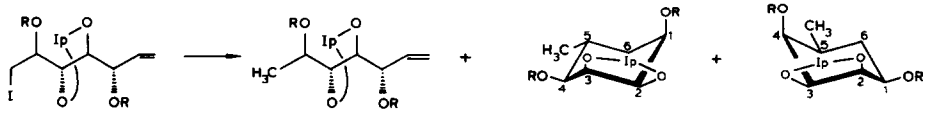
8

ative **7**. When **7** was treated with tributyltin hydride in refluxing benzene or toluene (standard conditions), reaction was slow and, after 24 h, ~80% of a nonpolar product had been formed, which was neither a deoxygenation nor a cylcisation product. The n.m.r. data of this product indicated **8** as the likely structure. The formation of **8** presumably involved an ionic mechanism, and may have reflected the structure of the bromide **7** and/or the pattern of substituents[6].

The corresponding 7-deoxy-7-iodo derivative **9** reacted at low concentrations with tributyltin hydride to give a mixture of the 5-carba cyclisation product **10** (30%) and the deoxygenation product **11** (10%) together with other products. The configuration of **10** was established on the basis of ^{1}H-n.m.r. data of its 2,3-diacetate (see Experimental), of which the $J_{4,5}$ value of 10.4 Hz clearly indicated the α-D-*allo* configuration.

Effect of the nature of the blocking groups. — It was considered possible that the benzyl ether groups adjacent to the intended reaction centres in **7** and **9** adversely affected the desired reactions. Therefore, the triol **12** and its 7-tosylate **13** (characterised as the 3,6-diacetate), the 7-deoxy-7-iodo derivative **14**, and its 3,5-diacetate **15** and

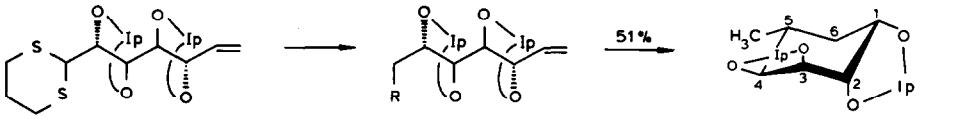
[Block A]



	D — allo	5a — carba — α — L — *allo*	5a-carba — β — D-*talo*
9 R = Bzl	**11** (10%)	**10** (30%)	—
14 R = H	**17** (17%)	**18** (34%)	**19** (26%)
15 R = Ac		**20** (87%)	—
16 R = Bz		**21** (80%)	—

3,5-dibenzoate **16** were synthesised and treated under the standard conditions. The results shown below indicate that the reactions of the diacetate **15** and dibenzoate **16** gave high yields of the respective cyclic derivatives **20** and **21**, and that the triol **14** gave a mixture of all three possible products (**17–19**). Compound **18** and **19** were characterised as the tetrabenzoates obtained by *O*-deisopropylidenation followed by benzoylation (see Experimental).

Radical cyclisation of L-manno- *and* D-gulo-*hept-1-enitol derivatives: formation of a seven-membered ring.* — The title compounds were available readily by the elimination–addition reaction[7] of 2-lithio-1,3-dithiane with 6-deoxy-6-iodo-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose followed by isopropylidenation, which yielded **22** (L-*manno*) and **26** (L-*gluco*). Each dithiane was converted into the aldehyde, which was reduced with borohydride to give the corresponding primary alcohols **23** (L-*manno*) and **27** (D-*gulo*), each characterised as the 7-acetate. Compound **23** was converted into the 7-deoxy-7-iodo derivative **24**, radical cyclisation of which yielded only one product (51%), namely, the 5a-carba-β-L-*altro* derivative **25**, characterised, after *O*-deisopropylidenation, as the tetrabenzoate. The modest yield of **25** indicated that the *manno* configuration favoured cyclisation less than the *allo* configuration.



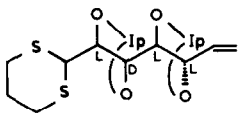
L — manno
22

L — manno
23 R = OH
24 R = I

5a — carba — β — L — altro
25

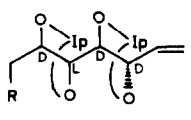
The D-*gulo*-hept-1-enitol derivative **27** was converted into the 7-deoxy-7-iodo derivative **28**, radical cyclisation of which also only gave one product in high yield (81%), but which was identified as the 6a-carbaseptanose derivative **29**, characterised, after *O*-deisopropylidenation, as the tetrabenzoate. In the reaction of **28**, the formation of a six-membered ring, in contrast to the sequence **24** → **25**, would have involved a *trans* orientation of one of the isopropylidene rings, probably an unfavoured arrangement. This view was supported by *O*-deisopropylidenation of **28** followed by conversion into the tetra-acetate **30**. Radical cyclisation of **30** gave an 88% yield of a 1:5 mixture of only six-membered β-D-*fuco* (**31**) and α-L-*altro* (**32**) products, characterised, after *O*-deacetylation, as the tetrabenzoates.

In another approach to *manno*-hept-1-enitol derivatives, 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose[8] (**33**) was subjected to a Wittig reaction to give the hept-1-enitol derivative **34**. Compound **34** was benzylated to give **35**, hydrolysis of which yielded the 3,4,6,7-tetrol **36** (characterised as the tetra-acetate), the 7-tosylate **37** (characterised as the 3,4,6-triacetate), the 7-deoxy-7-iodo derivative **38** (characterised as the 3,4,6-triacetate **39**), and the 7-deoxy-7-iodo-3,4-*O*-isopropylidene derivative **40** (characterised as



L — *gluco*

26

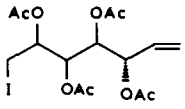


D — *gulo*

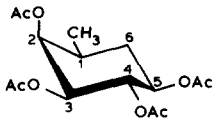
27 R = OH

28 R = I

29

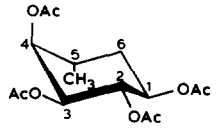


30



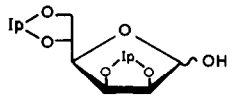
5a — carba — β — D — *fuco*

31



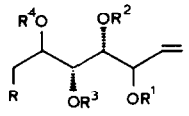
5a — carba — α — L — *altro*

32



D — *manno*

33

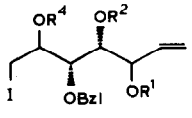


34 R^1, R^2 = Ip ; R^3 = H ; R^4 R = OIp

35 R^1, R^2 = Ip ; R^3 = Bzl ; R^4,R = OIp

36 R^1 = R^2 = R^4 = H ; R^3 = Bzl ; R = OH

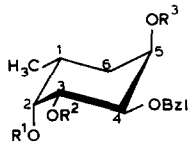
37 R^1 = R^2 = R^4 = H ; R^3 = Bzl ; R = OTs



38 R^1 = R^2 = R^3 = H

39 R^1 = R^2 = R^3 = Ac

40 R^1, R^2 = Ip ; R^3 = H

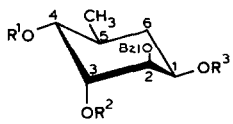


5a — carba — α — L — *fuco*

41 (36 %)

—

44 (8 %)

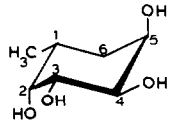


5a — carba — β — D — *altro*

42 (18 %)

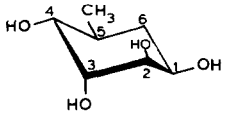
43 (36 %)

45 (48 %)



5a — carba — α — L — *fuco*

46

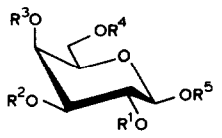


5a — carba — β — D — *altro*

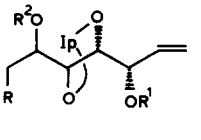
47

the 6-acetate). The results of radical cyclisations of **38–40** are shown in formulae **41–45**. Each cyclisation reaction occurred only to an extent of ~50% as found for the di-*O*-isopropylidene derivative **24**; for the triol **38**, the α-L-fuco product **41** preponderated. Compound **41** and **42** were characterised as the tribenzoates; **43**, after *O*-deacetylation, was characterised as the tribenzoate; and *O*-deisopropylidenation of **44** and **45** gave **41** and **42**, respectively. Compounds **41** and **42** were deblocked easily to give the respective 5a-carba derivatives **46** and **47**.

Radical cyclisation of a D-galacto-*hept-1-enitol derivative.* — The foregoing results indicated that the hept-1-enitol derivative most amenable to radical cyclisation was a 3,6-diester of a 7-deoxy-7-iodo-4,5-*O*-isopropylidene derivative (*cf.* **15**). Therefore, a compound of this type with the *galacto* configuration was synthesised from benzyl β-D-galactopyranoside[9] (**48**) via the 6-*O*-*tert*-butyldiphenylsilyl ether **49**, the 3,4-*O*-isopropylidene derivative **50**, and the diol **51** (characterised as the α and β 1,2-diacetates). A Wittig reaction of **51** gave the D-*galacto*-hept-1-entitol derivative **52** (60%), which was converted into 3,6-di-*O*-benzoyl-7-deoxy-7-iodo-4,5-*O*-isopropylidene-D-*galacto*-hept-1-enitol (**55**) via **53** (characterised as the 3,6,7-triacetate) and **54**.



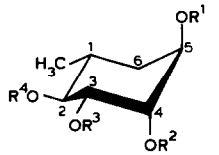
D — *galacto*



D — *galacto*

48 $R^1 = R^2 = R^3 = R^4 = H$; R^5 = Bzl
49 $R^1 = R^2 = R^3 = H$; $R^4 = {}^tBu\,Ph_2Si$; R^5 = Bzl
50 $R^1 = H$; R^2, R^3 = Ip ; $R^4 = {}^tBu\,Ph_2Si$; R^5 = Bzl
51 $R^1 = R^5 = H$; R^2, R^3 = Ip ; $R^4 = {}^tBu\,Ph_2Si$

52 $R^1 = R^2 = H$; $R = {}^tBu\,Ph_2SiO$
53 $R^1 = R^2 = H$; R = OH
54 $R^1 = R^2$ = Bz ; R = OTs
55 $R^1 = R^2$ = Bz ; R = I



5a — carba — α — L — *rhamno*

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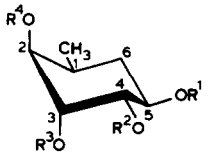
2 : 1



5a — carba — β — D — *gulo*

56 $R^1 = R^4 = H$; R^2, R^3 = Ip
58 $R^1 = R^2 = R^3 = R^4 = H$

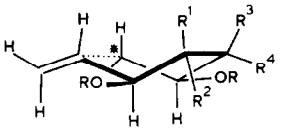
57 $R^1 = R^4 = H$; R^2, R^3 = Ip
59 $R^1 = R^2 = R^3 = R^4 = H$

Radical cyclisation of **55** gave a 90% yield of a 2:1 mixture of the α-L-*rhamno* (**56**) and the β-D-*gulo* (**57**) derivatives, each characterised, after *O*-deisopropylidenation, as the tetrabenzoate. Compounds **56** and **57** were deblocked easily to give the respective 5a-carba derivatives **58** and **59**.

DISCUSSION

According to the Hammond postulate[10], which applies to reactions in which a C–C bond is formed from a radical and a C = C bond, the conformation near to the transition state in an intramolecular cyclisation reaction is of extreme importance. The formation of a six-membered carbocycle from a 6-heptenyl radical in an exo process[11] is possible from chair- and boat-like transition states[12], with only a small difference in energy. Therefore, highly substituted 6-heptenyl radicals may be influenced strongly in the reaction pathways by the manner in which substituents affect the conformations that lead either to a chair-like or to a boat-like transition state. On the other hand, it is known[13], and can be demonstrated for example for **9** and **14–16** by n.m.r. spectroscopy, that conformations of the olefinic moiety are adopted in which the polar bond and the π-bond are parallel. At the side where the radical is generated, a polar bond (*e.g.*, at C-6) and the orbital that bears the radical have a parallel orientation, due to stabilising effects[14]. Thus, each end of the molecule has a predictable orientation. On the assumption that both O-3 and O-6 tend to adopt an equatorial orientation in the ring-forming process, then a relative *erythro* configuration at positions 3 and 6 in a hept-1-enitol should result in a boat-like transition state, whereas, for a *threo* configuration, a chair-like transition state should be preferred. This concept fits well with the results of the cyclisation reactions described above.

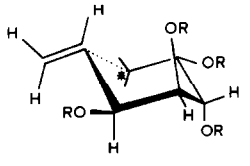
Thus, the *allo*-, *galacto*- and *gulo*-hept-1-enitol derivatives have the relative *erythro* orientation at C-3 and C-6 (Fig. 1). The highest selectivity occurred in the *allo* compound in which the 4,5-substituents avoid a rotation at the C-2–C-3 bond because of the large resulting O–C interaction. The *galacto* compound showed the same high tendency to cyclise, but with a significantly lower selectivity, because of the much smaller interactions of R^1 (= H) and the rotamer of C-2–C-3 with an axial orientation. The results for the *gulo* compound showed an increase in the selectivity, as expected.



D – *allo* $R^1 = R^3 = OR$, $R^2 = R^4 = H$ → 5a – carba – α – L – *allo*

D – *galacto* $R^1 = R^3 = H$; $R^2 = R^4 = OR$ → 5a – carba – α – L – *rhamno* + β – D – *gulo* (2 : 1)

D – *gulo* $R^1 = R^4 = OR$; $R^2 = R^3 = H$ → 5a – carba – α – L – *altro* + β – D – *fuco* (5 : 1)



L – *manno* → 5a – carba – β – L – *altro*

Fig. 1. Transition states of the D-*allo*, D-*galacto*, D-*gulo*, and L-*manno* hept-1-enitols.

The *manno*-hept-1-enitol derivatives have a relative *threo* configuration at C-3 and C-6. In a boat-like transition state, one of the oxygens will have an axial orientation, which can be avoided if the cyclisation occurs from a chair-like transition state, and *β-altro*-products should result, as was found (*α-altro* products should result from a boat-like transition state). These tendencies will be effected also by, for example, hydrogen bonding.

The data for the cyclisation of **9** and **14–16** reflect the effect of varying the blocking groups adjacent to the reaction centres. Compared to the unblocked compound **14**, ester groups at positions 3 and 6 increase the tendency to cyclisation, whereas benzyl ether groups have the opposite effect. These findings are consistent with the HSAB principle[15] in which radicals of the type discussed here should have a nucleophilic character. Their reactions with an olefin are accelerated if the olefin is influenced by electron-withdrawing groups (*e.g.*, in esters), whereas such electron-donating groups as ethers should have the opposite effect.

EXPERIMENTAL

General methods. — Reactions were monitored by t.l.c. on Silica Gel 60 F_{254} (Merck) with detection by charring with 0.2% naphthoresorcinol in ethanol–M sulphuric acid (1:1) or with ethanolic 10% sulfuric acid. Ordinary column chromatography was performed on Silica Gel 60 (70–230 mesh), and medium-pressure chromatography on Silica Gel 60 (230–400 mesh) at 0.2–0.6 MPa. Melting points were determined with a Leitz apparatus and are uncorrected. Optical rotations were determined with a Perkin–Elmer Model 243 polarimeter. ^{1}H-N.m.r. spectra were obtained with a Bruker

TABLE I

^{1}H-N.m.r. data[a] (δ in p.p.m., J in Hz) for the starting pyranoses and furanoses

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5A*	*H-5B*	*H-6A*	*H-6B*	*SiMe, ^{t}Bu, CMe_2, OH, PhCH, Ph*
2	d	d	d	dd	m		-	-	0.15, 0.92, 1.33, 1.49
	5.29	4.51	4.70	4.36	3.71–3.75				4.78(d)
49	d	dd	m 3.38–3.50 (3 H) and						1.06, 1.96, 3.04,
	4.23	3.69	m 3.86–3.94 (3 H)						4.54 (d), 4.85 (d), 7.18–7.76 (m)
50	d	dd	dd	dd	ddd	-	dd	dd	1.08, 1.34, 1.50, 2.52,
	4.23	3.60	4.05	4.24	3.86		3.97	4.01	4.58(d), 4.89(d), 7.26–7.80(m)

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6A}$	$J_{5,6B}$	$J_{6A,6B}$	$J_{1,OH}$	J_{CHPh}
2	0	5.8	2.2	2.2	-	-	-	11.8	-
49	7.8	9.4	[b]	[b]	[b]	[b]	[b]	-	11.6
50	8.2	7.4	5.4	2.0	6.0	7.0	9.8	-	11.6

[a] Measured in $CDCl_3$ (270 MHz). [b] Where values are missing, determination was not possible because of signal overlap of part of a multiplet.

TABLE II

^{1}H-N.m.r. data[a] (δ in p.p.m., J in Hz) for the enitols

Compound	*H-1A*	*H-1B*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-7A*	*H-7B*	*SiMe, $SiMe_2$, ^{t}Bu, CMe_2, OH, OAc, TsMe, CHPh, Ph*
3[d,e]	ddd	ddd	ddd	dddd	dd	dd	ddd	dd	dd	0.11, 0.92, 1.22, 1.29
	5.28	5.15	5.90	4.19	3.92	4.04	3.76	3.61	3.80	
5[d]	dd	dd	ddd	dd	dd	dd	ddd	dd	dd	0.06, 0.92, 1.34, 1.46, 4.44(d), 7.20–7.38(m)
	5.38	5.23	5.90	4.00	4.31	4.36	3.83	3.78	3.97	
6	dd	dd	ddd	dd	dd	dd		m		1.34, 1.46, 2.27(7-OH), 4.22(d), 4.42(d), 4.48(d), 4.56(d),
	5.41	5.29	5.87	4.00	4.28	4.37		3.74–3.88		7.14–7.42(m)
7[d]	dd	dd	ddd	dd	dd	dd	ddd	ddd	dd	1.35, 1.45, 4.24(d), 4.36(d), 4.53–4.59(m), 7.18–7.38(m)
	5.39	5.29	5.88	3.98	4.37	4.29	3.93	3.67	3.73	
9	dd	dd	ddd	dd		m	ddd	dd	dd	1.35, 1.45, 4.50(d), 4.56(d), 4.20–4.33(m), 7.17–7.39(m)
	5.39	5.20	5.88	3.93	4.20–4.33		3.45	3.50	3.55	
12[e]	d	d	ddd	dd	dd	dd	ddd	dd	dd	1.33, 1.41
	5.38	5.27	6.00	4.28	4.15	4.03	3.91	3.66	3.85	
14[e]	ddd	ddd	ddd	dddd	dd	dd	ddd	dd	dd	1.35, 1.40 •
	5.37	5,27	5.99	4.24	4.02	4.05	3.62	3.39	3.57	
15		m	ddd	m	dd	dd	ddd	dd	dd	1.37, 1.42, 2.07, 2.12
	5.29–5.25		5.91	5.29–5.42	4.29	4.33	4.48	3.53	3.62	
16	ddd	ddd	ddd	dddd	dd	dd	ddd	dd	dd	1.45, 1.51, 7.11–7.86(m)
	5.33	5.25	5.96	5.60	4.49	4.73	4.69	3.69	3.76	
24	d	d	ddd	dd	dd	dd	ddd	dd	dd	1.40, 1.44, 1.53
	5.42	5.37	6.07	4.69	4.18	3.66	3.94	3.24	3.33	
28	d	d	ddd	dd	dd	dd	ddd	dd	dd	1.40, 1.44, 1.53
	5.42	5.37	6.07	4.69	4.18	3.66	3.94	3.24	3.33	
30	dd	dd	ddd	dd	dd	dd	ddd	dd	dd	2.01, 2.05, 2.07, 2.09
	5.43	5.36	5.50	5.21	5.29	5.50	4.91	3.24	3.31	
34	ddd	ddd	ddd	dddd	dd	dd		m		1.35, 1.38, 1.42, 1.52, 2.25(d)
	5.39	5.33	6.10	4.70	4.38	3.45		3.88–4.14		
35	dd	dd	ddd	dd	dd	dd	ddd	dd	dd	1.35, 1.37, 1.40, 1.52, 4.69(d), 4.88(d), 7.18–7.46(m)
	5.35	5.26	5.98	4.63	4.19	3.73	4.18	4.01	4.06	
52	ddd	ddd	ddd	3.95–3.99(m), 4.31–4.39(m)			4.12(dd)	dd	dd	1.06, 1.37, 1.53, 3.29, 3.38, 7.32–7.71(m)
	5.39	5.24	5.92					3.71	3.79	
54	d	ddd	ddd	dd	dd	dd	ddd	dd	dd	1.37, 1.53, 2.38, 7.23–8.08(m)
	5.50	5.37	5.87	5.62	4.53	4.46	5.41	4.24	4.32	
55	d	d	ddd	dd	dd	dd	ddd	dd	dd	1.46, 1.62, 7.34–8.18(m)
	5.43	5.54	5.92	5.71	4.62	4.75	5.26	3.45	3.47	

Compound	$J_{1A,1B}$	$J_{1A,2}$	$J_{1B,2}$	$J_{1A,3}$	$J_{1B,3}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7A}$	$J_{6,7B}$	$J_{7A,7B}$	J_{CH_2}	J_{Ph}
3	1.4	10.4	17.2	1.4	1.4	5.8	9.2	5.4	9.4	5.6	2.8	10.2	-	-
5	1.8	17.2	10.2	-	-	8.0	6.0	6.6	6.0	5.2	2.0	10.8	11.6	-
6	1.6	17.2	10.2	-	-	7.8	7.2	5.8	6.0	[c]	[e]	[d]	11.4	-
7	1.8	17.2	10.2	-	-	8.0	6.6	6.2	6.4	4.2	2.8	10.4	11.6 11.2	-
9	1.8	17.4	10.2	-	-	8.0	5.6	[c]	6.4	3.0	3.8	11.0	10.6	-
12	-	10.4	17.0	-	-	6.0	9.0	5.4	9.2	5.8	2.6	11.2	-	-
14	1.4	10.4	17.0	1.4	1.4	6.0	9.0	5.4	8.6	5.8	2.6	10.2	-	-
15	-	17.0	10.6	-	-	6.8	5.6	5.6	7.8	3.6	3.2	11.0	-	-
16	1.0	10.6	17.0	1.0	1.0	6.2	7.6	5.0	8.8	2.6	3.0	11.0	-	-
24	-	9.8	17.0	-	-	8.6	7.0	2.0	7.8	5.2	4.8	10.8	-	-
28	-	9.8	17.0	-	-	8.6	7.0	2.0	7.8	5.2	4.8	10.8	-	-
30	1.0	10.2	17.0	-	-	7.6	6.6	4.2	6.0	5.8	5.0	11.0	-	-
34	2.6	17.2	10.2	1.0	1.0	7.6	7.6	1.4	[c]	[c]	[c]	[c]	-	$J_{5,OH}$ 8.0
35	1.4	10.2	17.2	-	-	7.6	6.2	4.2	3.6	8.0	6.0	8.0	11.6	-
52	1.4	10.4	17.0	1.4	1.4	5.8	[b]	[b]	[b]	7.0	5.8	9.8	-	3.2 7.2
54	-	10.2	17.2	-	-	7.2	7.6	6.4	3.4	6.2	5.2	10.2	-	-
55	-	10.2	17.2	-	-	7.4	8.4	6.4	2.6	8.4	4.8	9.6	-	-

[a] Determined for solutions in $CDCl_3$ (270 MHz), unless stated otherwise. [b] Determination was not possible. [c] Where values are missing, determination was not possible because of signal overlap of part of a multiplet. [d] At 400 MHz. [e] Determined for solutions in $CDCl_3$–CD_3OD.

TABLE III

^{1}H-N.m.r. data[a] (δ in p.p.m., J in Hz) for the cyclitols

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6A*	*H-6B*	CH_3
46	dddq	dd	dd	dd	ddd	ddd	ddd	d
	2.00	3.73	3.61	3.66	3.94	1.61	1.50	0.97
47		m		dd	dddq	ddd	ddd	d
		3.81–3.94		3.37	1.79	1.58	1.43	0.99
58	m	dd	dd	m		m		d
	1.53–1.86	3.25	3.60	3.79–3.89		1.53–1.86		1.00
59	dddq	dd	dd	dd	ddd	ddd	ddd	d
	2.00	3.61	3.87	3.53	3.68	1.56	1.40	0.97

Compound	$J_{1,2}$	$J_{1,6A}$	$J_{1,6B}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6A}$	$J_{5,6B}$	J_{5,CH_3}	$J_{6A,6B}$	J_{CH2Ph}	J_{1,CH_3}
46	2.4	12.2	4.4	2.6	9.9	2.4	2.6	3.4	-	14.0	-	7.0
47	[b]	6.2	11.4	[b]	2.8	10.4	4.0	12.2	6.4	12.4	-	-
58	10.0	[b]	[b]	9.4	3.2	[b]	[b]	[b]	-	[b]	-	6.4
59	2.8	4.0	13.0	3.6	3.2	9.6	4.8	11.2	-	12.4	-	6.8

[a] Determined for solutions in CD_3OD (270 MHz). [b] Where values are missing, determination was not possible because of signal overlap of part of a multiplet.

WM 270 (270 MHz) or WM 400 (400 MHz) spectrometer. The data for compounds illustrated by formulae are recorded in Tables I–III.

General procedures. — *(a) Acetylation.* To a solution of the substrate (corresponding to 1 equiv. of OH) in dry pyridine (3 mL) was added acetic anhydride (1.1 equiv.). The solution was kept overnight at room temperature, then concentrated *in vacuo*. Several portions of toluene were evaporated from the residue, which was then subjected to chromatography.

(b) Benzoylation. To a solution of the substrate (1 mmol, corresponding to 1 equiv. of OH) in dry pyridine (10 mL) was added benzoyl chloride (1.5 equiv.). The solution was kept for 3 h at room temperature, then diluted with water, and concentrated. Several portions of toluene were evaporated from the residue, a solution of which in dichloromethane was washed with aqueous sodium hydrogencarbonate and water, dried (Na_2SO_4), and concentrated. The residue was subjected to chromatography.

(c) Radical cyclisation. A solution of 1.5 mmol of tributyltin hydride and azobisisobutyronitrile (AIBN, catalytic amount) in dry benzene (3 mL) was added dropwise to a refluxing solution of 1 mmol of the 7-deoxy-7-iodohept-1-enitol derivative in dry benzene (*c* 0.01). After 1–2 h, the solution was cooled to room temperature, then concentrated, and the residue was subjected to chromatography.

(d) O-*Deacylation.* A solution of the ester in dry methanol was treated with a sufficient amount of sodium methoxide. When the reaction was complete, the solution was neutralised with Lewatit CNP (H^+) resin, filtered, and concentrated.

(e) Silylation. To a solution of 1 mmol of the substrate (corresponding to 1 equiv.

of OH) in dry *N,N*-dimethylformamide (10 mL) were added imidazole (2.5 mmol) and *tert*-butylchlorodimethylsilane (or *tert*-butylchlorodiphenylsilane) (1.2 mmol). When the reaction was complete, water was added, and the mixture was stirred for 30 min and then concentrated. A solution of the residue in ethyl acetate was washed with water, dried (Na_2SO_4), and concentrated, and the residue was subjected to chromatography.

5-O-tert-Butyldimethylsilyl-2,3-O-isopropylidene-D-ribofuranose (**2**). — Compound **1** (4 g, 12.2 mmol) was treated as in (*e*). Column chromatography (ethyl acetate–hexane, 1:10) of the product gave **2** (5.36 g, 83%), α,β-ratio 1:6 (n.m.r. data), m.p. 46° (crystallisation from hexane–ethyl acetate, 10:1), $[\alpha]_D^{20}$ −26° (*c* 1, methanol).

Anal. Calc. for $C_{14}H_{28}O_5Si$: C, 55.23; H, 9.27. Found: C, 55.79; H, 9.35.

7-O-tert-Butyldimethylsilyl-1,2-dideoxy-4,5-O-isopropylidene-D-allo-hept-1-enitol (**3**). — A M solution of vinylmagnesium bromide in tetrahydrofuran (60 mL) was added dropwise under nitrogen to a solution of **2** (3 g, 9.85 mmol) in dry tetrahydrofuran (100 mL). The mixture was stirred for 24 h at room temperature, the excess of reagent was decomposed by the addition of saturated aqueous NH_4Cl (30 mL), and the mixture was stirred for 1 h and then poured into ether (500 mL). The organic layer was washed with aqueous $NaHCO_3$ and water, the combined aqueous phases were extracted with ether, and the ether extract was dried ($MgSO_4$) and concentrated. Chromatography (hexane–*tert*–butyl methyl ether, 3:1) of the residue gave **3** (2.6 g, 79%), isolated as a colorless syrup, $[\alpha]_D^{20}$ −21.5° (*c* 1.6, methanol).

Anal. Calc. for $C_{16}H_{32}O_5Si$: C, 57.79; H, 9.70. Found: C, 58.07; H, 9.66.

3,6-Di-O-benzyl-7-O-tert-butyldimethylsilyl-1,2-dideoxy-4,5-O-isopropylidene-D-allo-hept-1-enitol (**5**). — To a stirred solution of **3** (2.5 g, 7.5 mmol) in dry *N,N*-dimethylformamide at 5° (40 mL) under nitrogen was added sodium hydride (0.54 g, 22.5 mmol). After 30 min, benzyl bromide (4 mL, 37.5 mmol) was added dropwise, and stirring was continued for 6 h at −5°, methanol (5 mL) was added, and the mixture was allowed to reach room temperature and then concentrated *in vacuo*. A solution of the residue in ether was washed with water, dried ($MgSO_4$), and concentrated. Chromatography (20:1 hexane–*tert*–butyl methyl ether) of the residue afforded syrupy **5** (2.41 g, 62%), $[\alpha]_D^{20}$ −13.5° (*c* 2.8, methanol).

Anal. Calc. for $C_{30}H_{44}O_5Si$: C, 70.27; H, 8.65. Found: C, 70.51; H, 8.78.

3,6-Di-O-benzyl-1,2-dideoxy-4,5-O-isopropylidene-D-allo-hept-1-enitol (**6**). — Compound **5** (2.41 g, 4.7 mmol) was desilylated by stirring with Bu_4NF (5 mmol, 5M solution in tetrahydrofuran) for 2 h. Water (0.5 mL) was added, the solvent was evaporated, and the residue was subjected to column chromatography (3:1 hexane–*tert*-butyl methyl ether) to give **6** (1.62 g, 81%), isolated as a colorless syrup, $[\alpha]_D^{20}$ −25° (*c* 4.9, methanol).

Anal. Calc. for $C_{24}H_{30}O_5$: C, 72.34; H, 7.59. Found: C, 72.60; H, 7.62.

3,6-Di-O-benzyl-7-bromo-1,2,7-trideoxy-4,5-O-isopropylidene-D-allo-hept-1-enitol (**7**). — A solution of **6** (1.1 g, 2.6 mmol) and tetrabromoethane (2.75 g, 7.8 mmol) in dry acetonitrile was heated at 60°. A solution of triphenylphosphine (2.46 g, 9.36 mmol) in dry tetrahydrofuran (3 mL) was added, the mixture was kept for 1 h at 60°, then concentrated *in vacuo*, and a solution of the residue in ether was filtered and concentrat-

ed. Chromatography (20:1 hexane–*tert*-butyl methyl ether) of the residue gave **7** (1.17 g, 92%), isolated as a colorless syrup, $[\alpha]_D^{20}$ −29° (*c* 1.6, methanol).

Anal. Calc. for $C_{24}H_{29}BrO_4$: C, 62.48; H, 6.34; Br, 17.32. Found: C, 62.24; H, 6.37; Br, 16.81.

*4,7-Anhydro-3,6-di-*O*-benzyl-1,2-dideoxy-*D-allo*-hept-1-enitol* (**8**). — Compound **7** (100 mg, 0.2 mmol) was treated as in (*c*). Chromatography (8:1 hexane–ethyl acetate) of the product gave **8**. ^{1}H-N.m.r. data (270 MHz, $CDCl_3$; it was not possible to identify all of the signals): δ 2.73 (d, 1 H, *J* 6.0 Hz, OH), 3.84 (dd, 1 H, *J* 9.2 and 4.6 Hz), 3.9–3.97 (m, 2 H), 4.00 (dd, 1 H, *J* 9.2 and 5.0 Hz), 4.07 (dd, 1 H, *J* 9.8 and 5.0 Hz), 4.16 (dd, 1 H, 10.8 and 5.2 Hz), 4.42 (d, 1 H, *J* 11.8 Hz, C*H*$_2$Ph), 4.57 (d, 1 H, *J* 11.6 Hz, C*H*$_2$Ph), 4.62 (d, 1 H, *J* 11.6 Hz, C*H*$_2$Ph), 4.64 (d, 1 H, *J* 11.8 Hz, C*H*$_2$Ph), 5.34 (dd, 1 H, $J_{1B,2}$ 16.6, $J_{1A,1B}$ 1.6 Hz, H-1B), 5.36 (dd, 1 H, $J_{1A,2}$ 10.8 Hz, H-1A), 5.86 (ddd, 1 H, $J_{2,3}$ 7.2 Hz, H-2), 7.18–7.45 (m, 10 H, 2 Ph).

*3,6-Di-*O*-benzyl-1,2,7-trideoxy-7-iodo-4,5-*O*-isopropylidene-*D-allo*-hept-1-enitol* (**9**). — To a solution of **6** (250 mg, 0.63 mmol) in dry toluene (7.5 mL) were added imidazole (102 mg, 1.5 mmol), triphenylphosphine (393 mg, 1.5 mmol), and iodine (239 mg, 0.94 mmol). The mixture was stirred for 2 h at 80°, then cooled to room temperature, silica gel (1–2 g) was added, and the mixture was concentrated. The residue was extracted with ether and the extract was concentrated. Chromatography (20:1 hexane–ethyl acetate) of the residue gave **9** (254 mg, 79%), m.p. 36°, $[\alpha]_D^{20}$ −28.5° (*c* 1.3, methanol).

Anal. Calc. for $C_{24}H_{29}IO_4$: C, 56.70; H, 5.75; I, 24.96. Found: C, 56.95; H, 5.80; I, 25.28.

*1*L*-(1,2,3,4/5)-1,4-Di-*O*-benzyl-2,3-*O*-isopropylidene-5-C-methyl-1,2,3,4-cyclohexanetetrol (1,4-di-*O*-benzyl-6-deoxy-2,3-*O*-isopropylidene-5a-carba-α-*L*-allopyranose)* (**10**) *and 3,6-di-*O*-benzyl-1,2,7-trideoxy-4,5-*O*-isopropylidene-*D-allo*-hept-1-enitol* (**11**). — Compound **9** (300 mg, 0.59 mmol) was treated as in (*c*). Chromatography (hexane, 10:1 hexane–ethyl acetate, 5:1 hexane–ethyl acetate) of the product gave **10** (68 mg, 30%) and **11** (22 mg, 10%), isolated as colorless syrups.

The 1,4-diacetate of **10** had $[\alpha]_D^{20}$ −66° (*c* 0.45, methanol). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 0.99 (d, 3 H, J_{5,CH_3} 6.6 Hz, CH_3), 1.14 (ddd, 1 H, $J_{1,6B}$ 2.6, $J_{5,6B}$ 12.0, $J_{6A,6B}$ 14.0 Hz, H-6B), 2.05 (ddd, 1 H, $J_{1,6A}$ 3.6, $J_{5,6A}$ 3.8 Hz, H-6A), 2.06 and 2.09 (2 s, each 3 H, CMe_2), 2.33 (dddq, 1 H, $J_{4,5}$ 10.4 Hz, H-5), 3.08 (dd, 1 H, $J_{3,4}$ 3.0 Hz, H-4), 3.81 (ddd, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 4.33, 4.63, 4.58, and 4.63 (4 d, each 1 H, *J* 11.6 Hz and 12.2 Hz, 2 C*H*$_2$Ph), 4.85 (dd, 1 H, $J_{2,3}$ 3.2 Hz, H-2), 5.73 (dd, 1 H, H-3), 7.21–7.44 (m, 10 H, 2 Ph).

Anal. Calc. for $C_{25}H_{30}O_6$: C, 70.4; H, 7.09. Found: C, 70.3; H, 7.16.

Compound **11** had $[\alpha]_D^{20}$ −25.5° (*c* 0.6, methanol). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 1.26 (d, 3 H, $J_{6,Me}$ 6.2 Hz, CH_3), 1.34 and 1.46 (2 s, each 3 H, CMe_2), 3.82 (dq, 1 H, $J_{6,Me}$ 6.2, $J_{5,6}$ 6.0 Hz, H-6), 3.95 (dd, 1 H, $J_{2,3}$ 8.0, $J_{3,4}$ 6.4 Hz, H-3), 4.21 (dd, 1 H, $J_{4,6}$ 6.0 Hz, H-5), 4.22 and 4.30 (2 d, each H, *J* 11.4 Hz, C*H*$_2$Ph), 4.31 (dd, 1 H, H-4), 4.5 and 4.54 (2 d, each 1 H, *J* 11.4 Hz, C*H*$_2$Ph), 5.22 (dd, 1 H, $J_{1,2}$ 17.2, $J_{1A,1B}$ 1.8 Hz, H-1A), 5.39 (dd, 1 H, $J_{1B,2}$ 10.2, H-1B), 5.88 (ddd, 1 H, H-2), 7.14–7.41 (m, 10 H, 2 Ph).

Anal. Calc. for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 75.58; H, 8.01.

*1,2-Dideoxy-4,5-*O*-isopropylidene-*D*-allo-hept-1-enitol* (**12**). — Compound **3** (2 g, 6 mmol) was desilylated as described for **5**. Chromatography (1:1 hexane–ethyl acetate) of the product gave **12** (1.05 g, 80%), m.p. 71°, $[\alpha]_D^{20}$ −38° (*c* 1.0, methanol).

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

To a stirred solution of **12** (150 mg, 0.69 mmol) in pyridine (5 mL) was added trityl chloride (428 mg, 1.5 mmol). The solution was kept for 2 h at 80°, then concentrated. Chromatography (5:1 hexane–*tert*-butyl methyl ether) of the residue gave **4** (230 mg, 72%), m.p. 153°, $[\alpha]_D^{20}$ +17° (*c* 0.6, chloroform); lit.[4] m.p. 153°, $[\alpha]_D^{20}$ +19.4° (chloroform).

*1,2-Dideoxy-4,5-*O*-isopropylidene-7-*O*-p-toluenesulfonyl-*D*-allo-hept-1-enitol* (**13**). — To a solution of **12** (1.33 g, 6.1 mmol) in dry pyridine (2.4 mL) and dry dichloromethane at 0° was added a solution of tosyl chloride (2.3 g, 12 mmol) in dry dichloromethane (4.5 mL). The mixture was stirred for 18 h at 0°, dichloromethane (300 mL) was added, and the mixture was washed with water, dried, and concentrated. Column chromatography (3:1 hexane–ethyl acetate) of the residue gave **13** (1.71 g, 75%), isolated as a colorless syrup.

The 3,6-diacetate of **13** had $[\alpha]_D^{20}$ −2° (*c* 1.6, methanol). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 1.31 and 1.35 (2 s, each 3 H, CMe_2), 2.00 and 2.05 (2 s, each 3 H, 2 Ac), 2.43 (s, 3 H, Ts*Me*), 4.21 (dd, 1 H, $J_{6,7A}$ 3.2, $J_{7A,7B}$ 11.0 Hz, H-7A), 4.24 (dd, 1 H, $J_{3,4}$ 5.8, $J_{4,5}$ 5.8 Hz, H-4), 4.38 (dd, 1 H, $J_{6,7B}$ 2.2 Hz, H-7B), 4.39 (dd, 1 H, $J_{5,6}$ 8.6 Hz, H-5), 4.95 (ddd, 1 H, H-6), 5.26–5.37 (m, 2 H, H-1A,1B), 5.86 (ddd, 1 H, $J_{1A,2}$ 17, $J_{1B,2}$ 10.2 Hz, H-2), 5.26–5.37 (m, 1 H, H-3), 7.30–7.43 and 7.73–7.86 (m, 4 H, Ph).

Anal. Calc. for $C_{21}H_{28}O_9S$: C, 55.25; H, 6.18; S, 7.02. Found: C, 55.61; H, 6.09; S, 7.50.

*1,2,7-Trideoxy-7-iodo-4,5-*O*-isopropylidene-*D*-allo-hept-1-enitol* (**14**). — To a stirred solution of **13** (1.71 g, 4.60 mmol) in dry tetrahydrofuran (23 mL) was added sodium iodide (1.37 g, 9.20 mmol) and tetrabutylammonium iodide (0.3 g). The mixture was kept for 20 h at 40°, chloroform (300 mL) was added, and the slurry was filtered, washed with water, dried, and concentrated. Column chromatography (6:1 hexane–ethyl acetate) of the residue gave **14** (1.09 g, 72%), isolated as a syrup, $[\alpha]_D^{20}$ −17° (*c* 2.6, methanol).

Anal. Calc. for $C_{10}H_{17}IO_4$: C, 36.60; H, 5.22; I, 38.67. Found: C, 36.51; H, 5.81; I, 39.12.

*3,5-Di-*O*-acetyl-1,2,7-trideoxy-7-iodo-4,5-*O*-isopropylidene-*D*-allo-hept-1-enitol* (**15**). — Acetylation of **14** (200 mg, 0.61 mmol) as in (*a*), with column chromatography (10:1 hexane–ethyl acetate) of the product, gave **15** (231 mg, 92%), isolated as a syrup, $[\alpha]_D^{20}$ −28° (*c* 2.7, methanol).

Anal. Calc. for $C_{14}H_{21}IO_6$: C, 40.79; H, 5.13; I, 30.79. Found: C, 41.15; H, 5.27; I, 30.20.

*3,6-Di-*O*-benzoyl-1,2,7-trideoxy-7-iodo-4,5-*O*-isopropylidene-*D*-allo-hept-1-enitol* (**16**). — Compound **14** (200 mg, 0.61 mmol) was treated as in (*b*). Column chromatography (10:1 hexane–ethyl acetate) of the product gave **16** (295 mg, 90%), isolated as a syrup, $[\alpha]_D^{20}$ −43° (*c* 3.2, methanol).

Anal. Calc. for $C_{24}H_{25}IO_6$: C, 53.74; H, 4.70; I, 23.66. Found: C, 54.03; H, 4.71; I, 24.1.

*1,2,7-Trideoxy-4,5-O-isopropylidene-*D-allo-*hept-1-enitol* (**17**) *1*L-*(1,2,3,4/5)-2,3-O-isopropylidene-5-C-methyl-1,2,3,4-cyclohexanetetrol (6-deoxy-2,3-O-isopropylidene-5a-carba-α-*L-*allopyranose* (**18**) *and 1*L-*(1,2,3,4,5/0)-2,3-O-isopropylidene-5-C-methyl-1,2,3,4-cyclohexanetetrol (6-deoxy-2,3-O-isopropylidene-5a-carba-β-*D-*talopyranose* (**19**). — Compound **14** (175 mg, 0.53 mmol) was treated as in (*c*). Column chromatography (1:1 hexane–ethyl acetate) of the product gave syrupy **17** (18 mg, 17%), **18** (36 mg, 34%), and **19** (28 mg, 26%).

Compound **17** had $[\alpha]_D^{20}$ −27° (*c* 1.8, methanol). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 1.33 (d, 3 H, $J_{6,7}$ 6.0 Hz, H-7,7,7), 1.34 and 1.39 (2 s, each 3 H, CMe_2), 3.47 (d, 1 H, $J_{3,OH}$ 2.8 Hz, HO-3), 3.62 (d, 1 H, $J_{6,OH}$ 3.0 Hz, HO-6), 3.93 (dd, 1 H, *J* 9.0 and 5.0 Hz, H-4 or H-5), 4.01 (dd, 1 H, *J* 9.0 and 5.0 Hz, H-4 or H-5), 4.04 (ddd, 1 H, $J_{5,6}$ 9.0, $J_{6,7}$ 6.0 Hz, H-6), 4.31 (ddddd, 1 H, $J_{3,4}$ 9.0, $J_{2,3}$ 5.8, $J_{1A,3}$ 1.4, $J_{1B,3}$ 1.4 Hz, H-3), 5.29 (ddd, 1 H, $J_{1A,2}$ 10.4 Hz, H-1A), 5.38 (ddd, 1 H, $J_{1B,2}$ 17.0, $J_{1A,1B}$ 1.4 Hz, H-1B), 6.04 (ddd, 1 H, H-2).

Anal. Calc. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 60.20; H, 8.09.

O-Deisopropylidenation of **18** with aqueous 80% acetic acid and then benzoylation gave 1L-(1,2,3,4/5)-1,2,3,4-tetra-*O*-benzoyl-5-*C*-methyl-1,2,3,4-cyclohexanetetrol (1,2,3,4-tetra-*O*-benzoyl-6-deoxy-5a-carba-α-L-allopyranose), m.p. 71°, $[\alpha]_D^{20}$ −68° (*c* 1.7, methanol), ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 1.13 (d, 3 H, J_{5,CH_3} 6.6 Hz, CH_3), 1.78 (ddd, 1 H, $J_{1,6B}$ 2.6, $J_{5,6B}$ 12.0. $J_{6A,6B}$ 15.0 Hz, H-6B), 2.39 (ddd, 1 H, $J_{1,6A}$ 3.6, $J_{5,6A}$ 4.0 Hz, H-6A), 2.81 (dddq, 1 H, $J_{4,5}$ 10.8 Hz, H-5), 5.21 (dd, 1 H, $J_{3,4}$ 3.0 Hz, H-4), 5.57 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 3.0 Hz, H-2), 5.78 (ddd, 1 H, H-1), 6.10 (dd, 1 H, H-3), 7.10–8.11 (m, Ph).

Anal. Calc. for $C_{35}H_{30}O_8$: C, 72.65; H, 5.23. Found: C, 72.68; H, 5.32.

Likewise, *O*-deisopropylidenation of **19** and then benzoylation gave syrupy 1L-(1,2,3,4,5/0)-1,2,3,4-tetra-*O*-benzoyl-5-*C*-methyl-1,2,3,4-cyclohexanetetrol-(1,2,3,4-tetra-*O*-benzoyl-6-deoxy-5a-carba-β-D-talopyranose, $[\alpha]_D^{20}$ +41° (*c* 1.2, methanol). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 1.18 (d, 1 H, J_{5,CH_3} 6.6 Hz, CH_3), 2.04 (ddd, 1 H, $J_{1,6B}$ 4.0, $J_{5,6B}$ 12.8, $J_{6A,6B}$ 12.0 Hz, H-6B), 2.24 (dddq, 1 H, $J_{5,6A}$ 2.8, $J_{4,5}$ 3.0 Hz, H-5), 2.39 (ddd, 1 H, $J_{1,6A}$ 11.6 Hz, H-6A), 5.43 (ddd, 1H, $J_{1,2}$ 3.2 Hz, H-1), 5.50 (dd, 1 H, $J_{3,4}$ 4.0 Hz, H-4), 5.79 (dd, 1 H, $J_{2,3}$ 2.6 Hz, H-2), 6.10 (dd, 1 H, H-3), 7.20–8.14 (m, Ph).

Anal. Calc. for $C_{35}H_{30}O_8$: C, 72.65; H, 5.23. Found: C, 72.91; H, 5.29.

*1*L-*(1,2,3,4/5)-1,4-Di-*O*-acetyl-2,3-*O*-isopropylidene-5-*C*-methyl-1,2,3,4-cyclohexanetetrol (1,4-di-*O*-acetyl-6-deoxy-2,3-*O*-isopropylidene-5a-carba-α-*L*-allopyranose)* (**20**). — Compound **15** (195 mg, 0.47 mmol) was treated as in (*c*). Column chromatography (4:1 hexane–ethyl acetate) of the product gave syrupy **20** (110 mg, 87%). *O*-Deisopropylidenation of **20**, then benzoylation, gave the same product as derived from **18**.

*1*L-*(1,2,3,4/5)-1,4-Di-*O*-benzoyl-2,3-*O*-isopropylidene-5-*C*-methyl-1,2,3,4-cyclohexanetetrol (1,4-di-*O*-benzoyl-6-deoxy-2,3-*O*-isopropylidene-5a-carba-α-*L*-allopyranose)* (**21**). — Compound **16** (216 mg, 0.4 mmol) was treated as in (*c*). Column chromatography (12:1 hexane–ethyl acetate) of the product gave **21** (172 mg, 80%), isolated as a

colorless syrup. *O*-Deisopropylidenation of **21**, then benzoylation, gave the same product as derived from **18**.

1,2-Dideoxy-3,4:5,6-di-O-*isopropylidene*-L-manno-*hept-1-enitol* (**23**). — A solution of **22**[7] (400 mg, 1.15 mmol) in acetone–water (4:1, 23 mL) was boiled under reflux with 2,4,6-collidine (1.53 mL, 11.5 mmol) and methyl iodide (0.71 mL, 11.5 mmol) for 6 h, then concentrated. A solution of the residue in ethanol–water (2:1, 23 mL) was stirred with sodium borohydride (220 mg, 5.8 mmol) for 12 h. $NaHCO_3$ (0.5 g) was added, and the mixture was stirred for 1 h, then concentrated. The residue was partitioned between dichloromethane and water, the aqueous layer was extracted with dichloromethane, and the combined organic solutions were dried ($MgSO_4$) and concentrated. Column chromatography (1:1 hexane–*tert*-butyl methyl ether) of the residue gave **23** (0.92 g, 70%), isolated as a colorless syrup, $[\alpha]_D^{20}$ +11° (*c* 0.8, methanol).

Anal. Calc. for $C_{13}H_{22}O_5$: C, 60.45; H, 8.58. Found: C, 60.20; H, 8.51.

^{1}H-N.m.r. data for the 7-acetate of **23** (270 MHz, C_6D_6): δ 1.25, 1.26, 1.45, 1.49, and 1.71 (5 s, each 3 H, 2 CMe_2 and Ac), 3.96 (dd, 1 H, $J_{6,7A}$ 5.4, $J_{7A,7B}$ 10.8 Hz, H-7A), 4.13–4.30 (m, 3 H, H-5,6,7B), 4.43 (dd, 1 H, $J_{2,3}$ 8.0, $J_{3,4}$ 6.4 Hz, H-3), 5.05 (d, 1 H, $J_{1B,2}$ 17.0 Hz, H-1B), 5.18 (d, 1 H, $J_{1A,2}$ 10.2 Hz, H-1A), 5.91 (ddd, 1 H, H-2).

1,2,7-Trideoxy-7-iodo-3,4:5,6-di-O-*isopropylidene*-L-manno-*hept-1-enitol* (**24**). — Compound **23** (88 mg, 0.34 mmol) was treated with imidazole, triphenylphosphine, and iodine as described in the preparation of **9**. Chromatography (ether) of the product gave a syrup, which, after further column chromatography (9:1 hexane–*tert*-butyl methyl ether), gave **24** (104 mg, 83%), m.p. 57°, $[\alpha]_D^{20}$ +75.5° (*c* 0.3, methanol).

Anal. Calc. for $C_{13}H_{21}IO_4$: C, 42.41; H, 5.75; I, 34.36. Found: C, 42.40; H, 5.68; I, 34.15.

*1*D-*(1,2,5/3,4)-1,2:3,4-Di*-O-*isopropylidene-5*-C-*methyl-1,2,3,4-cyclohexanetetrol (6-deoxy-1,2:3,4-di*-O-*isopropylidene-5a-carba-β*-L-*altropyranose)* (**25**). — Compound **24** (95 mg, 0.26 mmol) was treated as in (*c*). Column chromatography (hexane, 6:1 hexane–*tert*-butyl methyl ether) of the product gave syrupy **25** (31 mg, 51%).

O-Deisopropylidenation of **25** with aqueous 80% acetic acid followed by benzoylation gave 1D-(1,2,5/3,4)-1,2,3,4-tetra-*O*-benzoyl-5-*C*-methyl-1,2,3,4-cyclohexanetetrol (6-deoxy-1,2,3,4-tetra-*O*-benzoyl-5a-carba-*β*-L-altropyranose, $[\alpha]_D^{20}$ +45° (*c* 1.1, chloroform). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 1.20 (d, 3 H, J_{5,CH_3} 6.8 Hz, CH_3), 2.05 (ddd, 1 H, $J_{1,6B}$ 11.2, $J_{5,6B}$ 10.8, $J_{6A,6B}$ 13.0 Hz, H-6B), 2.34 (ddd, 1 H, $J_{1,6A}$ 4.6, $J_{5,6A}$ 4.0 Hz, H-6A), 2.60 (dddq, 1 H, $J_{4,5}$ 10.4 Hz, H-5), 5.48 (dd, 1 H, $J_{3,4}$ 2.0 Hz, H-4), 5.73 (ddd, 1 H, $J_{1,2}$ 2.4 Hz, H-1), 5.90–5.97 (m, 2 H, H-2,3), 7.27–8.16 (m, Ph).

Anal. Calc. for $C_{35}H_{30}O_8$: C, 72.65; H, 5.23. Found: C, 72.76; H, 5.28.

1,2-Dideoxy-3,4:5,6-di-O-*isopropylidene*-D-gulo-*hept-1-enitol* (**27**) — Compound **26**[7] (1.76 g, 5.1 mmol) was treated as described above for **22**. Column chromatography (1:1 hexane–*tert*-butyl methyl ether) of the product gave **27** (0.92 g, 70%), isolated as a colorless syrup, $[\alpha]_D^{20}$ +83° (*c* 1.0, methanol).

^{1}H-N.m.r. data of the 7-acetate of **27** (270 MHz, $CDCl_3$): δ 1.35, 1.37, 1.42, and 1.49 (s, each 3 H, 2 CMe_2, Ac), 2.05 (s, 3 H, Ac), 3.71 (dd, 1 H, $J_{4,5}$ 2.2, $J_{5,6}$ 8.2 Hz, H-5), 4.06 (dd, 1 H, $J_{6,7A}$ 5.8, $J_{7A,7B}$ 11.6 Hz, H-7A), 4.10 (dd, 1 H, $J_{3,4}$ 7.0 Hz, H-4), 4.20 (ddd, 1

H, $J_{6,7B}$ 3.0 Hz, H-6), 4.29 (dd, 1 H, H-7B), 4.68 (dd, 1 H, $J_{2,3}$ 8.6 Hz, H-3), 5.35 (d, 1 H, $J_{1B,2}$ 17.0 Hz, H-1B), 5.41 (d, 1 H, $J_{1A,2}$ 10.0 Hz, H-1A); 6.06 (ddd, 1 H, H-2).

Anal. Calc. for $C_{13}H_{22}O_5$: C, 60.45; H, 8.58. Found: C, 60.17; H, 8.49.

*1,2,7-Trideoxy-7-iodo-3,4:5,6-di-*O*-isopropylidene-*D-gulo*-hept-1-enitol* (**28**). — Compound **27** (0.5 g, 1.9 mmol) was treated with imidazole, triphenylphosphine, and iodine as described above for the preparation of **9**. Column chromatography (9:1 hexane–*tert*-butyl methyl ether) of the product gave **27** (0.579 g, 83%), m.p. 57°, $[\alpha]_D^{20}$ + 75.5° (*c* 0.3, methanol).

Anal. Calc. for $C_{13}H_{21}IO_4$: C, 42.41; H, 5.75; I, 34.36. Found: C, 42.40; H, 5.68; I, 34.15.

*1D-(1,2,4/3)-1,2:3,4-Di-*O*-isopropylidene-1,2,3,4-cycloheptanetetrol* (**29**). — Compound **28** (90 mg, 0.24 mmol) was treated as in (*c*). Column chromatography (hexane, 6:1 hexane–*tert*-butyl methyl ether) of the product gave **29** (47 mg, 81%).

O-Deisopropylidenation of **29** with aqueous 80% acetic acid followed by benzoylation gave 1D-(1,2,4/3)-1,2,3,4-tetra-*O*-benzoyl-1,2,3,4-cycloheptanetetrol as a colorless syrup, $[\alpha]_D^{20}$ + 35° (*c* 0.75, methanol). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 2.0–2.42 (m, 6 H, H-5,5,6,6,7,7), 5.53 (ddd, 1 H, $J_{3,4}$ 7.2, $J_{4,5A}$ 3.3, $J_{4,5B}$ 8.4 Hz, H-4), 5.73 (ddd, 1 H, $J_{1,2}$ 1.5, $J_{1,7A}$ 3.2, $J_{1,7B}$ 7.2 Hz, H-1), 5.76 (dd, 1 H, $J_{2,3}$ 7.0 Hz, H-2), 6.07 (dd, 1 H, H-3), 7.25–8.16 (m, 20 H, 4 Ph).

Anal. Calc. for $C_{35}H_{30}O_8$: C, 72.65; H, 5.23. Found: C, 72.90; H, 5.33.

*3,4,5,6-Tetra-*O*-acetyl-1,2,7-trideoxy-7-iodo-*D-gulo*-hept-1-enitol* (**30**). — To a solution of **28** (579 mg, 1.57 mmol) in aqueous 80% acetic acid (7 mL) were added three drops of trifluoroacetic acid. The solution was stirred overnight at room temperature, then concentrated *in vacuo*, and toluene was distilled several times from the residue, which was acetylated as in (*a*). Column chromatography (6:1 hexane–ethyl acetate) of the product gave **30** (412 mg, 57%), m.p. 112°, $[\alpha]_D^{20}$ + 15° (*c* 1.1, methanol).

Anal. Calc. for $C_{15}H_{21}IO_8$: C, 39.49; H, 4.64; I, 27.82. Found: 39.51; H, 4.71; I, 27.45.

*1D-(1,2,3,5/4)-2,3,4,5-Tetra-*O*-acetyl-1-*C*-methyl 2,3,4,5-cyclohexanetetrol (1,2,3,4-tetra-*O*-acetyl-5a-carba-β-*D*-fucopyranose)* (**31**) *and 1*L*-(1,3,4/2,5)-1,2,3,4-tetra-*O*-acetyl-5-*C*-methyl-1,2,3,4-cyclohexanetetrol (1,2,3,4-tetra-*O*-acetyl-6-deoxy-5a-carba-α-*L*-altropyranose)* (**32**). — Compound **30** (200 mg, 0.44 mmol) was treated as in (*c*). Column chromatography (3:1 hexane–ethyl acetate) of the product failed to separate the isomeric products **31** and **32** present in the ratio 1:5 (^{1}H-n.m.r. data). The colorless syrupy mixture (130 mg, 88%) was *O*-deactylated and then benzoylated, to give a mixture of the tetrabenzoates with $[\alpha]_D^{20}$ + 79.5° (*c* 2.25, chloroform). ^{1}H-N.m.r. data: tetrabenzoate of **31** (270 MHz, $CDCl_3$), δ 1.10 (d, 3 H, J_{1,CH_3}) 6.6 Hz, CH_3, 5.43 (ddd, 1 H, $J_{5,6A}$ 4.6, $J_{5,6B}$ 11.4, $J_{4,5}$ 10.0 Hz, H-5), 5.52 (dd, 1 H, $J_{2,3}$ 3.0, $J_{3,4}$ 10.4 Hz, H-3), 5.85 (dd, 1 H, $J_{1,2}$ 3.0 Hz, H-2), 6.15 (dd, 1 H, H-4), 7.18–8.15 (m, Ph) (the signals of H-1,6A,6B could not be identified due to overlap with the signals for the major isomer); tetrabenzoate of **32** (270 MHz, $CDCl_3$), δ 1.36 (d, 3 H, J_{5,CH_3} 7.2 Hz, CH_3), 2.16 (ddd, 1 H, $J_{1,6B}$ 4.8, $J_{5,6B}$ 5.0, $J_{6A,6B}$ 13.6 Hz, H-6B), 2.30 (ddd, 1 H, $J_{1,6A}$ 9.0, $J_{5,6A}$ 4.6 Hz, H-6A), 2.62 (dddq, 1 H, $J_{4,5}$ 5.4 Hz, H-5), 5.58 (ddd, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 5.61 (dd, 1 H, $J_{3,4}$ 3.0 Hz, H-4), 5.77 (dd, 1 H, $J_{2,3}$ 8.2 Hz, H-3), 6.07 (dd, 1 H, H-2), 7.18–8.15 (m, Ph).

Anal. Calc. for $C_{35}H_{30}O_8$: C, 72.65; H, 5.23. Found: C, 72.87; H, 5.30.

1,2-Dideoxy-3,4:6,7-di-O-*isopropylidene*-D-manno-*hept-1-enitol* (**34**). — To a stirred solution of methyltriphenylphosphonium iodide (62 g, 154 mmol) in dry tetrahydrofuran (650 mL) at −5° to −10° under N_2 was added dropwise 1.6M butyl-lithium in hexane (86 mL, 138 mmol). After 1 h, a solution of **33**[8] (10 g, 38.4 mmol) in tetrahydrofuran (70 mL) was added dropwise, and the stirred solution was kept overnight at room temperature. The reaction was quenched after cooling by the addition of saturated aqueous NH_4Cl (5 mL) and acetone (15 mL). After 1 h, the solution was decanted, silica gel (40 g) was added, and the mixture was concentrated. The silica gel was eluted with *tert*-butyl methyl ether and the eluate was concentrated. Column chromatography (6:1 hexane–ethyl acetate) of the residue gave **34** (6.65 g, 67%), isolated as a colorless syrup, $[\alpha]_D^{20}$ −39° (*c* 2.5, methanol).

Anal. Calc. for $C_{13}H_{22}O_5$: C, 60.45; H, 8.58. Found: C, 60.83; H, 8.67.

5-O-*Benzyl-1,2-dideoxy-3,4:6,7-di*-O-*isopropylidene*-D-manno-*hept-1-enitol* (**35**). — To a stirred solution of **34** (3.52 g, 13.6 mmol) in dry *N,N*-dimethylformamide (58 mL) at 0° under N_2 was added sodium hydride (653 mg, 21.8 mmol). After 1 h, benzyl bromide (2.59 mL, 21.8 mmol) was added dropwise at 0° and the mixture was stirred overnight at room temperature. Methanol was added, the mixture was concentrated under high vacuum, and a solution of the residue in ether was washed with water, dried ($MgSO_4$), and concentrated. Column chromatography (5:1 hexane–ethyl acetate) of the residue gave **35** (3.97 g, 84%), isolated as a colorless syrup, $[\alpha]_D^{20}$ −13° (*c* 2.8 methanol).

Anal. Calc. for $C_{20}H_{28}O_5$: C, 68.94; H, 8.10. Found: C, 68.63; H, 7.97.

5-O-*Benzyl-1,2-dideoxy*-D-manno-*hept-1-enitol* (**36**). — A solution of **35** (3.97 g, 11.4 mmol) in acetic acid (18 mL) was stirred for 20 h at room temperature, then concentrated *in vacuo*, and toluene was evaporated several times from the residue to give **36** (3.0 g, 98%), isolated as a colorless syrup.

The 3,4,6,7-tetra-acetate of **36** was a colorless syrup, $[\alpha]_D^{20}$ +28.0° (*c* 2.9, methanol). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 2.00, 2.02, 2.05, and 2.06 (4 s, each 3 H, 4 Ac), 3.90 (dd, 1 H, $J_{4,5}$ 3.4, $J_{5,6}$ 7.0 Hz, H-5), 4.15 (dd, 1 H, $J_{6,7A}$ 5.4, $J_{7A,7B}$ 12.4 Hz, H-7A), 4.51–4.60 (m, 3 H), 5.15 (ddd, 1 H, $J_{6,7B}$ 2.8 Hz, H-6), 5.27 (dd, 1 H, $J_{3,4}$ 7.6 Hz, H-4), 5.32 (d, 1 H, $J_{1B,2}$ 17.0 Hz, H-1B), 5.41 (d, 1 H, $J_{1A,2}$ 10.2 Hz, H-1A), 5.47 (dd, 1 H, H-3), 5.77 (ddd, 1 H, H-2), 7.23–7.43 (m, Ph).

Anal. Calc. for $C_{22}H_{28}O_9$: C, 60.54; H, 6.47. Found: C, 60.50; H, 6.52.

5-O-*Benzyl-1,2-dideoxy-7*-O-p-*toluenesulfonyl*-D-manno-*hept-1-enitol* (**37**). — Compound **36** (5.1 g, 19 mmol) was treated with tosyl chloride–pyridine as described for **12**. Column chromatography (1:1 hexane–ethyl acetate) of the product gave **37** (4.21 g, 52%), isolated as a colorless syrup. The 3,4,6-triacetate of **37** was a colorless syrup, $[\alpha]_D^{20}$ +22° (*c* 3, methanol). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 1.95 (s, 6 H, 2 Ac), 2.09 (s, 3 H, Ac), 2.42 (s, 3 H, Ts*Me*), 4.00 (dd, 1 H, $J_{4,5}$ 2.9, $J_{5,6}$ 8.4 Hz, H-5), 4.24 (dd, 1 H, $J_{6,7A}$ 3.0, $J_{7A,7B}$ 11.2 Hz, H-7A), 4.29 (dd, 1 H, $J_{6,7B}$ 3.0 Hz, H-7B), 4.46 and 4.51 (2 d, each 1 H, *J* 10.6 Hz, PhCH_2), 5.19 (dd, 1 H, $J_{3,4}$ 8.0, $J_{4,5}$ 2.9 Hz, H-4), 5.30 (dd, 1 H, $J_{1A,1B}$ 1.2, $J_{1B,2}$ 17.2 Hz, H-1B), 5.38 (dd, $J_{1A,2}$ 10.2 Hz, H-1A), 5.43 (dd, $J_{2,3}$ 7.3 Hz, H-3), 5.72 (ddd, 1 H, H-2), 7.17–7.38 and 7.72–7.82 (2 m, Ph).

Anal. Calc. for $C_{27}H_{32}O_{10}S$: C, 59.11; H, 5.88; S, 5.84. Found: C, 59.40; H, 5.96; S, 6.14.

*5-O-Benzyl-1,2,7-trideoxy-7-iodo-*D*-manno-hept-1-enitol* (**38**). — Compound **37** (4 g, 9.47 mmol) was treated with iodine as described for **13**. Column chromatography (1:1 hexane–ethyl acetate) of the product gave **38** (2.78 g, 78%). The 3,4,6-triacetate (**39**) of **38** was a colorless syrup, $[\alpha]_D^{20}$ + 20° (*c* 0.46, methanol).

Anal. Calc. for $C_{20}H_{25}IO_7$: C, 47.63; H, 5.00; I, 25.16. Found: C, 47.71; H, 5.10. I, 25.45.

*5-O-Benzyl-1,2,7-trideoxy-7-iodo-3,4-O-isopropylidene-*D*-manno-hept-1-enitol* (**40**). — To a solution of **38** (645 mg, 1.7 mmol) in dry *N,N*-dimethylformamide (13 mL) were added isopropenyl methyl ether (0.19 mL, 2.05 mmol) and *p*-toluenesulfonic acid (~ 1 mg). The mixture was stirred for 6 h at room temperature, then neutralised with conc. ammonia, and concentrated under dimished pressure. A solution of the residue in dichloromethane was washed with water, dried ($MgSO_4$), and concentrated. Column chromatography (6:1 hexane–ethyl acetate) of the residue gave **40** (259 mg, 36%), isolated as a colorless syrup. The 6-acetate of **40** was a colorless syrup, $[\alpha]_D^{20}$ + 29° (*c* 3.7, methanol). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 1.37 and 1.50 (2 s, each 3 H, CMe_2), 2.10 (s, 3 H, Ac), 3.40 (dd, 1 H, $J_{6,7A}$ 8.2, $J_{7A,7B}$ 11.2 Hz, H-7A), 3.66 (dd, 1 H, $J_{5,6}$ 3.6, $J_{4,5}$ 4.4 Hz, H-5), 3.69 (dd, 1 H, $J_{6,7B}$ 3.0 Hz, H-7B), 4.29 (dd, 1 H, $J_{3,4}$ 6.6 Hz, H-4), 4.62 (dddd, 1 H, $J_{2,3}$ 7.2, $J_{1A,3}$ 1.2, $J_{1B,3}$ 1.2 Hz, H-3), 4.68 and 4.76 (2 d, 2 H, *J* 11.4 Hz, CH_2Ph), 4.27 (ddd, 1 H, H-6), 5.29 (ddd, 1 H, $J_{1A,1B}$ 1.2, $J_{1B,2}$ 17.2 Hz, H-1B), 5.39 (ddd, 1 H, $J_{1A,2}$ 10.2 Hz, H-1A), 5.96 (ddd, 1 H, H-2).

Anal. Calc. for $C_{19}H_{25}IO_5$: C, 49.58; H, 5.47; I, 27.57. Found: C, 49.22; H, 5.41; I, 28.01.

*1*L*-(1,2,3/4,5)-4-O-Benzyl-1-C-methyl-2,3,4,5-cyclohexanetetrol (2-O-benzyl-5a-carba-α-*L*-fucopyranose)* (**41**) *and 1*L*-(1,2,5/3,4)-2-O-benzyl-5-C-methyl-1,2,3,4-cyclohexanetetrol (2-O-benzyl-6-deoxy-5a-carba-β-*D*-altropyranose)* (**42**). — Compound **38** (500 mg, 1.32 mmol) was treated as in (*c*). Column chromatography (1:1 hexane–ethyl acetate, ethyl acetate) of the product gave **41** (121 mg, 36%) and **42** (60 mg, 18%), isolated as colorless syrups.

The 2,4,5-tribenzoate of **41** was a colorless syrup, $[\alpha]_D^{20}$ − 160° (*c* 1.5, chloroform). ^{1}H-N:m.r. data (270 MHz, $CDCl_3$): δ 1.00 (d, 3 H, J_{1,CH_3} 6.6 Hz, CH_3), 1.81–2.08 (m, 2 H, H-6A,6B), 2.43–2.59 (m, 1 H, $J_{1,2}$ 5.8 Hz, H-1), 4.12 (dd, 1 H, $J_{3,4}$ 10.2, $J_{4,5}$ 3.0 Hz, H-4), 4.59 and 4.72 (2 d, 2 H, *J* 12.2 Hz, PhCH_2), 5.74 (dd, 1 H, $J_{2,3}$ 3.0 Hz, H-3), 5.82 (m, 1 H, H-5), 5.91 (dd, 1 H, H-2), 7.11–8.22 (m, 15 H, 3 Ph).

Anal. Calc. for $C_{35}H_{33}O_7$: C, 74.32; H, 5.88. Found: C, 74.49; H, 5.89.

The 1,3,4-tribenzoate of **42** was a colorless syrup, $[\alpha]_D^{20}$ + 14° (*c* 1.1, chloroform). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 1.09 (d, 3 H, J_{5,CH_3} 6.6 Hz, CH_3), 1.98–2.19 (m, 2 H, H-6A,6B), 2.49 (dddq, 1 H, $J_{4,5}$ 11.0, $J_{5,6A}$ 5.0, $J_{5,6B}$ 11.2 Hz, H-5), 4.18 (dd, 1 H, $J_{1,2}$ 3.0, $J_{2,3}$ 4.2 Hz, H-2), 5.40 (dd, 1 H, $J_{3,4}$ 3.0 Hz, H-4), 4.78 and 4.92 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 5.50 (ddd, 1 H, $J_{1,6A}$ 10.8, $J_{1,6B}$ 5.4 Hz, H-1), 5.90 (dd, 1 H, H-3), 7.11–8.11 (m, 15 H, 3 Ph).

Anal. Calc. for $C_{35}H_{33}O_7$: C, 74.32; H, 5.88. Found: C, 74.41; H, 5.82.

1L-(1,2,5/3,4)-1,3,4-Tri-O-acetyl-2-O-benzyl-5-C-methyl-1,2,3,4-cyclohexanetetrol (1,3,4-tri-O-acetyl-2-O-benzyl-6-deoxy-5a-carba-β-D-altropyranose) (**43**). — Compound **39** (173 mg, 0.34 mmol) was treated as in (*c*). *O*-Deacetylation of **43** as in (*d*), and then benzoylation gave a tribenzoate identical (31 mg, 36%) to that derived from **42**.

1L-(1,2,3/4,5)-4-O-Benzyl-2,3-O-isopropylidene-1-C-methyl-2,3,4,5-cyclohexanetetrol (2-O-benzyl-3,4-O-isopropylidene-5a-carba-α-L-fucopyranose) (**44**) *and 1L-(1,2,5/3,4)-2-O-benzyl-3,4-O-isopropylidene-5-C-methyl-1,2,3,4-cyclohexanetetrol (2-O-benzyl-6-deoxy-3,4-O-isopropylidene-5a-carba-β-D-altropyranose)* (**45**). — Compound **40** (259 mg, 0.62 mmol) was treated as in (*c*). The product, a mixture of **44** and **45**, was *O*-deisopropylidenated with aqueous 80% acetic acid. The solution was concentrated and toluene was evaporated from the residue. Column chromatography (1:1 hexane–ethyl acetate, ethyl acetate) of the residue gave **41** (13 mg, 8%) and **42** (75 mg, 48%), isolated as colorless syrups.

1-L-(1,2,3/4,5)-1-C-Methyl-2,3,4,5-cyclohexanetetrol (5a-carba-α-L-fucopyranose) (**46**). — A solution of **41** (68 mg, 0.27 mmol) in dry methanol (5 mL) was hydrogenated in the presence of 10% Pd/C (60 mg) at atmospheric pressure for 12 h, then filtered, and concentrated *in vacuo*. Column chromatography (3:1 chloroform–ethanol) of the residue gave **46** (35 mg, 77%), m.p. 115°, $[\alpha]_D^{20}$ −58° (*c* 1, methanol).

Anal. Calc. for $C_7H_{14}O_4$: C, 51.84; H, 8.70. Found: C, 51.61, H, 8.76.

1L-(1,2,5/3,4)-5-C-Methyl-1,2,3,4-cyclohexanetetrol (6-deoxy-5a-carba-β-D-altropyranose) (**47**). — Compound **42** (35 mg, 0.14 mmol) was hydrogenated as for **41**, to give **47** (19 mg, 84%), m.p. 178°, $[\alpha]_D^{20}$ +41° (*c* 1, methanol).

Anal. Calc. for $C_7H_{14}O_4$: C, 51.81; H, 8.70. Found: C, 52.03; H, 8.91.

Benzyl 6-O-tert-butyldiphenylsilyl-β-D-galactopyranoside (**49**). — Benzyl β-D-galactopyranoside (**48**; 3.9 g, 14.4 mmol) was silylated as in (*e*). Column chromatography (ethyl acetate) of the product gave **49** (6.21 g, 85%), m.p. 45°, $[\alpha]_D^{20}$ −27° (*c* 2.15, methanol).

Anal. Calc. for $C_{29}H_{36}O_6Si$: C, 68.47; H, 7.13. Found: C, 68.50; H, 7.11.

Benzyl 6-O-tert-butyldiphenylsilyl-3,4-O-isopropylidene-β-D-galactopyranoside (**50**). — To a solution of **49** (6.21 g, 12.2 mmol) in dry acetone (100 mL) were added $CaSO_4$ (~ 1 g) and *p*-toluenesulfonic acid (~ 10 mg). The mixture was stirred for 15 h at room temperature, neutralised with conc. ammonia, filtered, and concentrated *in vacuo*. Column chromatography (3:1 hexane–ethyl acetate +2‰ of triethylamine) of the residue gave **50** (5.25 g, 78%), m.p. 38°, $[\alpha]_D^{20}$ −10° (*c* 3.25, methanol).

Anal. Calc. for $C_{32}H_{40}O_6Si$: C, 70.04; H, 7.35. Found: C, 69.91; H, 7.31.

6-O-tert-Butyldiphenylsilyl-3,4-O-isopropylidene-D-galactopyranose (**51**). — A solution of **50** (6.3 g, 11.5 mmol) in dry methanol (500 mL) was hydrogenated in the presence of 10% Pd/C (5 g) and $NaHCO_3$ (5 g) at atmospheric pressure for 24 h, then filtered, and concentrated *in vacuo*. A solution of the residue in dichloromethane (500 mL) was washed with water, dried ($MgSO_4$), and concentrated to yield **51** (4.9 g, 93%) as an α,β-mixture, m.p. 51°, $[\alpha]_D^{20}$ +35° (*c* 0.2, chloroform). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$) for the diacetates: α anomer, δ 1.04 (s, 9 H, ^{t}Bu), 1.37 and 1.62 (2 s, each 3 H, 2Ac), 2.05–2.10 (2 s, each 3 H, 2 Ac), 3.83 (dd, 1 H, $J_{5,6A}$ 6.0 Hz, $J_{6A,6B}$ 10 Hz, H-6A), 3.96

(dd, 1 H, $J_{5,6B}$ 8.2 Hz, H-6B), 4.18 (ddd, 1 H, $J_{4,5}$ 2.4 Hz, H-5), 4.33 (dd, 1 H, $J_{3,4}$ 5.6, $J_{2,3}$ 8.0 Hz, H-3), 4.44 (dd, 1 H, H-4), 5.06 (dd, 1 H, $J_{1,2}$ 3.8 Hz, H-2), 6.17 (d, 1 H, H-1), 7.30–7.74 (m, Ph); *β* anomer, *δ* 1.04 (s, 9 H, ^{t}Bu), 1.50 and 1.55 (2 s, each 3 H, 2Ac), 2.05–2.10 (2 s, each 3 H, 2 Ac), 3.87 (dd, 1 H, $J_{5,6A}$ 5.6 Hz, $J_{6A,6B}$ 9.8 Hz, H-6A), 3.95 (dd, 1 H, $J_{5,6B}$ 7.8 Hz, H-6B), 4.04 (ddd, 1 H, $J_{4,5}$ 2.0 Hz, H-5), 4.22 (dd, 1 H, $J_{3,4}$ 5.6, $J_{2,3}$ 7.2 Hz, H-3), 4.39 (dd, 1 H, H-4), 5.09 (dd, 1 H, $J_{1,2}$ 8.4 Hz, H-2), 5.55 (d, 1 H, H-1), 7.30–7.74 (m, Ph).

Anal. Calc. for $C_{25}H_{34}O_6Si$: C, 65.47; H, 7.47. Found: C, 65.51; H, 7.46.

7-O-tert-Butyldiphenylsilyl-1,2-dideoxy-4,5-O-isopropylidene-D-galacto-*hept-1-enitol* (**52**). — To a stirred solution of methyltriphenylphosphonium iodide (22.7 g, 56.49 mmol) in dry tetrahydrofuran (180 mL) at −5° under N_2 was added dropwise 1.6M butyl-lithium in hexane (31.8 mL, 51 mmol). After 1 h, a solution of **51** (3.56 g, 7.76 mmol) in dry tetrahydrofuran was added dropwise. The stirred solution was kept for 36 h at room temperature, then worked-up as described for **34**. Column chromatography (3:1 hexane–ethyl acetate) of the product gave **52** (2.13 g, 60%), isolated as a colorless syrup, $[\alpha]_D^{20}$ −5° (*c* 0.8, methanol).

Anal. Calc. for $C_{26}H_{36}O_5Si$: C, 68.39; H, 7.95. Found: C, 68.57; H, 8.04.

1,2-Dideoxy-4,5-O-isopropylidene-D-galacto-*hept-1-enitol* (**53**). — Compound **52** (2.0 g, 4.38 mmol) was desilylated as described for **5**. Column chromatography (60:1 ethyl acetate–methanol) of the product gave **53** (870 mg, 91%), isolated as a colorless syrup.

The 3,6,7-triacetate of **53** was a colorless syrup, $[\alpha]_D^{20}$ +9.5° (*c* 1.2, methanol). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): *δ* 1.37 and 1.53 (each s, each 3 H, CMe_2), 2.05, 2.09, and 2.17 (each s, each 3 H, 3 Ac), 4.10 (dd, 1 H, $J_{6,7A}$ 7.2, $J_{7A,7B}$ 11.8 Hz, H-7A), 4.17 (dd, 1 H, $J_{4,5}$ 6.4, $J_{5,6}$ 2.8 Hz, H-5), 4.23 (dd, 1 H, $J_{6,7B}$ 5.2 Hz, H-7B), 4.29 (dd, 1 H, $J_{3,4}$ 8.4 Hz, H-4), 5.22 (ddd, 1 H, H-6), 5.35 (dd, 1 H, $J_{2,3}$ 7.8, $J_{3,4}$ 8.4 Hz, H-3), 5.39 (d, 1 H, $J_{1B,2}$ 17.6 Hz, H-1B), 5.51 (d, 1 H, $J_{1A,2}$ 10.6 Hz, H-1A), 5.78 (ddd, 1 H, H-2).

Anal. Calc. for $C_{16}H_{24}O_8$: C, 55.81; H, 7.02. Found: C, 55.52; H, 7.10.

3,6-Di-O-benzoyl-1,2-dideoxy-4,5-O-isopropylidene-7-O-p-toluenesulfonyl-D-galacto-*hept-1-enitol* (**54**). — Compound **53** (0.44 g, 2.02 mmol) was treated with tosyl chloride–pyridine as described for **12**. After 20 h, benzoyl chloride was added, the solution was stirred for 1 h, water was added, the solvents were evaporated, and toluene was evaporated several times from the residue. A solution of the residue in dichloromethane was washed with saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated. Column chromatography (6:1 hexane–ethyl acetate) of the residue gave **54** (0.825 g, 70%), isolated as a colorless syrup, $[\alpha]_D^{20}$ −17° (*c* 1, methanol).

Anal. Calc. for $C_{31}H_{32}O_9S$: C, 64.10; H, 5.55; S, 5.52. Found: C, 64.30; H, 5.58; S, 5.17.

3,6-Di-O-benzoyl-1,2,7-trideoxy-7-iodo-4,5-O-isopropylidene-D-galacto-*hept-1-enitol* (**55**). — Compound **54** (0.7 g, 1.2 mmol) was treated with sodium iodide as described for **13**. Column chromatography (12:1 hexane–ethyl acetate) of the product gave **55** (0.52 g, 81%), isolated as a colorless syrup, $[\alpha]_D^{20}$ +18° (*c* 1, methanol).

Anal. Calc. for $C_{24}H_{25}IO_6$: C, 53.74; H, 4.70; I, 23.66. Found: C, 53.66; H, 4.61; I, 23.92.

1L-(1,3,4/2,5)-3,4-O-Isopropylidene-1-C-methyl-2,3,4,5-cyclohexanetetrol (2,3-O-isopropylidene-5a-carba-α-L-rhamnopyranose) (**56**) *and 1D-(1,2,5/3,4)-3,4-O-isopropylidene-1-C-methyl-2,3,4,5-cyclohexanetetrol (6-deoxy-2,3-O-isopropylidene-5a-carba-β-D-gulopyranose)* (**57**). — Compound **55** (330 mg, 0.615 mmol) was treated as in (*c*) and the product was deacylated as in (*d*). Column chromatography (10:1 toluene–ethanol) of the product gave **56** (52 mg, 46%) and **57** (26 mg, 23%), isolated as colorless syrups.

O-Deisopropylidenation of **56** with aqueous 80% acetic acid and then benzoylation gave 1-L-(1,3,4/2,5)-2,3,4,5-tetra-*O*-benzoyl-1-*C*-methyl-2,3,4,5-cyclohexanetetrol (1,2,3,4-tetra-*O*-benzoyl-5a-carba-α-L-rhamnopyranose), m.p. 165°, $[\alpha]_D^{20}$ + 48° (*c* 1, chloroform). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 1.14 (d, 3 H, J_{1,CH_3} 6.4 Hz, CH_3), 2.03 (dd, 1 H, $J_{1,6B}$ 12.6, $J_{5,6B}$ 2.6, $J_{6A,6B}$ 15.0 Hz, H-6B), 2.26 (ddd, 1 H, $J_{1,6A}$ 4.0, $J_{5,6A}$ 2.6 Hz, H-6A), 2.42 (dddq, 1 H, $J_{1,2}$ 10.4 Hz, H-1), 5.51 (ddd, 1 H, $J_{4,5}$ 3.6 Hz, H-5), 5.72 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 5.86 (dd, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 5.91 (dd, 1 H, H-4), 7.18–8.23 (m, 20 H, 4 Ph).

Anal. Calc. for $C_{35}H_{30}O_8$: C, 75.65; H, 5.23. Found: C, 75.69; H, 5.26.

Likewise, **57** gave 1-D-(1,2,5/3,4)-2,3,4,5-tetra-*O*-benzoyl-1-*C*-methyl-2,3,4,5-cyclohexanetetrol (1,2,3,4-tetra-*O*-benzoyl-6-deoxy-5a-carba-β-D-gulopyranose), isolated as a colorless syrup, $[\alpha]_D^{20}$ −41.5° (*c* 1, chloroform). ^{1}H-N.m.r. data (270 MHz, $CDCl_3$): δ 1.10 (d, 3 H, J_{1,CH_3} 6.8 Hz, CH_3), 1.98 (ddd, 1 H, $J_{1,6B}$ 12.6, $J_{5,6B}$ 11.0, $J_{6A,6B}$ 12.8 Hz, H-6B), 2.16 (dddq, 1 H, $J_{1,2}$ 2.8, $J_{1,6A}$ 3.8 Hz, H-1), 2.37 (ddd, 1 H, $J_{5,6A}$ 4.6 Hz, H-6A), 5.9 (dd, 1 H, $J_{2,3}$ 2.8 Hz, H-2), 5.76 (ddd, 1 H, $J_{4,5}$ 9.8 Hz, H-5), 5.84–5.93 (m, 2 H, H-3,4), 7.20–8.20 (m, 20 H, 4 Ph).

Anal. Calc. for $C_{35}H_{30}O_8$: C, 75.65; H, 5.23. Found: C, 75.41; H, 5.29.

1L-(1,3,4/2,5)-1-C-Methyl-2,3,4,5-cyclohexanetetrol (5a-carba-α-L-rhamnopyranose) (**58**). — The foregoing benzoate (36 mg, 0.18 mmol) derived from **56** was *O*-debenzoylated as in (*d*). Column chromatography (3:1 chloroform–ethanol) of the product gave **58** (23 mg, 78%), isolated as a colorless syrup, $[\alpha]_D^{20}$ + 5.9° (*c* 1, methanol).

Anal. Calc. for $C_7H_{14}O_4$: C, 51.84; H, 8.70. Found: C, 52.16; H, 8.79.

1D-(1,2,5/3,4)-1-C-Methyl-2,3,4,5-cyclohexanetetrol (6-deoxy-5a-carba-β-D-gulopyranose) (**59**). — The benzoate derived from **57** was *O*-debenzoylated to give **59**, m.p. 132°, $[\alpha]_D^{20}$ − 52° (*c* 1, methanol).

Anal. Calc. for $C_7H_{14}O_4$: C, 51.84; H, 8.70. Found: C, 51.91; H, 8.60.

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REFERENCES

1 G. E. McCasland, S. Furuta, and L. J. Durham, *J. Org. Chem.*, 31 (1966) 1516–1521.
2 T. Suami, *Pure Appl. Chem.*, 59 (1987) 1509–1520.
3 J. Stoddart, *Stereochemistry of Carbohydrates*, Wiley–Interscience, New York, 1971, pp. 93–97.

4 J. G. Buchanan, A. D. Dunn, and A. R. Edgar, *J. Chem. Soc., Perkin Trans. 1*, (1975) 1191–1200.
5 C. S. Wilcox and L. M. Tomasco, *J. Org. Chem.*, 50 (1985) 546–547.
6 C. Wentrup, *Reaktive Zwischenstufen*, 1st edn., Vol. 1, Thieme Verlag, Stuttgart, 1979.
7 J. B. Lenfers, Dissertation, University of Hamburg, 1988.
8 O. Th. Schmidt, *Methods Carbohydr. Chem.*, 2 (1963) 318–319.
9 A. Stoffyn and P. Stoffyn, *J. Org. Chem.*, 32 (1967) 4001–4006; A. Levy, H. M. Flowers, and N. Sharon, *Carbohydr. Res.*, 4 (1967) 305–311.
10 G. S. Hammond, *J. Am. Chem. Soc.*, 77 (1955) 334–338.
11 J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, (1976) 734–736.
12 A. L. J. Beckwith and C. H. Schiesser, *Tetrahedron*, 41 (1985) 3925–3941; D. C. Spellmeyer and K. N. Houk, *J. Org. Chem.*, 52 (1987) 959–974.
13 E. W. Garbisch, *J. Am. Chem. Soc.*, 86 (1964) 5561–5564; M. Barfield, *ibid.*, 93 (1971) 1066–1071; J. Schwentner, Diplom, University of Hamburg, 1976.
14 D. H. R. Barton, W. Hartwig, and W. B. Motherwell, *J. Chem. Soc., Chem. Commun.*, (1982) 447–448; K. S. Gröninger, K. J. Jäger, and B. Giese, *Liebigs Ann. Chem.*, (1987) 731–732; K. S. Chen and J. K. Kochi, *J. Am. Chem. Soc.*, 96 (1974) 1383–1392; A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, (1972) 786–794, 794–802.
15 R. G. Pearson, *J. Org. Chem.*, 54 (1989) 1423–1430.