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Synthesis of 3,6-dideoxy-4-*C*-(4^1-hydroxyethyl)hexopyranoses (yersinioses) from 1,6-anhydro-β-D-glucopyranose

Vladimir A. Zubkov, Raisa P. Gorshkova, Yuriy S. Ovodov,
Pacific Institute of Bioorganic Chemistry, Far East Branch of the Academy of Sciences of the U.S.S.R., Vladivostok (U.S.S.R.)

Alexander F. Sviridov, and Alexander S. Shashkov
N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

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ABSTRACT

A series of isomers of 3,6-dideoxy-4-*C*-(4^1-hydroxyethyl)-D-hexopyranose (yersiniose), structural components of the O-specific polysaccharides from the *Yersinia* genus, have been synthesised from 1,6-anhydro-β-D-glucopyranose (levoglucosan).

INTRODUCTION

A new branched monosaccharide, yersiniose A, identified on the basis of spectral data as 3,6-dideoxy-4-*C*-(4^1-hydroxyethyl)-D-*xylo*-hexose, has been found[1] as a component of the O-specific polysaccharide of *Yersinia pseudotuberculosis* serovar VI. A similar monosaccharide (yersiniose B) with spectral characteristics different from those of yersiniose A has been isolated[2] from the lipopolysaccharide of *Y. enterocolitica* serovar O:4,32. The ^{13}C-n.m.r. data showed that, in the polymer, yersiniose A was β whereas yersiniose B was α. The ^{1}H-n.m.r. data for the free monosaccharides indicated the 2,4^1,5-substituents to be equatorial but the absolute configuration could not be assigned.

The monosaccharide (**1**) under study has three chiral centres (2,4^1,5) and one pseudo-chiral centre (C-4). The chemical (but not the stereochemical) identity of the 4-substituents results in partial degeneracy of the stereoisomerism and 3,6-dideoxy-4-*C*-(4^1-hydroxyethyl)hexose may exist as only 8 stereoisomers, namely DDL, DLD, LDL, LLD, DDD, LDD, DLL, and LLL (for C-2, *pro-S* at C-4^1, and *pro-R* at C-5, respectively). Only the isomers which are D at C-2 and/or C-4 need be considered.

As C-4 becomes chiral in the pyranose ring, each of the remaining stereoisomers can form two diastereomeric pyranose forms from either *pro-S* or *pro-R* centres and each may exist in the $^1C_4$ or $^4C_1$ conformation. Thus, the total isomers for the above six forms are 24. However, only three conformers comply with experimental requirements, namely, DLD at *pro-R* closure and the $^4C_1$ conformation **2**, DDD at *pro-R* closure and the $^4C_1$ conformation **3**, and LLD at *pro-S* closure and the $^1C_4$ conformation **4**.

Since the monosaccharides are incorporated in the polysaccharides in the α or β forms and differ in their spectra, only **2** and **3**, which differ only in the configuration at

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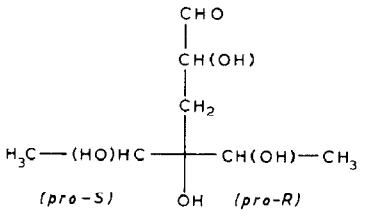
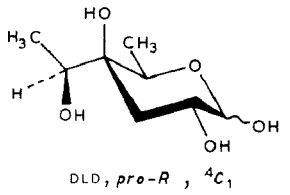
C-4[1], conform to the above criteria. Thus, it was necessary to perform stereodirected syntheses of **2** and **3** in order to resolve the question of the structures of yersinioses A and B.

Paulson and Sinnwell[4] have described two monosaccharides that were isomeric at C-4[1] but had the inverted configuration at C-4. However, their scheme does not allow synthesis of **2** and **3**. We now describe the synthesis of **2** and **3** from 1,6-anhydro-β-D-glucopyranose (**5**, levoglucosan).



1



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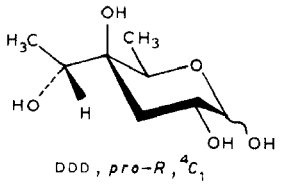

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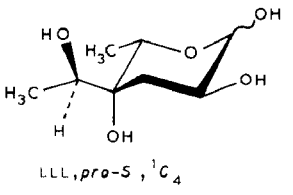

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RESULTS AND DISCUSSION

Levoglucosan (**5**) was chosen as the starting compound since the tosylate **6** has been described[5]. Mesylates of type **7** are known to yield epoxides of type **8** that can be reduced regioselectively[6] to yield 3-deoxy derivatives **9** in which HO-2 and HO-4 can be differentiated. Thus, an easy route to the keto derivative **12** through the sequence **9**→**11** is provided. The 4-keto derivative may be utilised in several ways[7]. The conversion of ketone **12** into **2** and **3** requires deoxygenation at C-6 and the introduction of the branch at C-4 in the form of an acetyl residue. Reduction of the keto group at C-4[1] in these stereoisomers will give two isomeric alcohols and, thus, it appears possible to obtain all stereoisomers at C-4 and C-4[1], starting from **12**.

All stages in the synthesis of **12** gave good yields and the structures of the intermediate compounds were confirmed by the n.m.r. data (the ^{1}H- and ^{13}C-n.m.r. data for the compounds described herein are given in Tables I–VI).

The only difficulty encountered was the removal of the *O*-allyl group in **10**. Treatment[8] of **10** in methyl sulfoxide with potassium *tert*-butoxide gave 8% of the olefin **13** instead of the expected alcohol **11**. However the *O*-allyl group in **10** could be

TABLE I

^{1}H-N.m.r. data (δ in p.p.m., J in Hz) for **7–13**

Compound	*H-1* $J_{1,2}$	*H-2* $J_{2,3ax}$	*H-3* $J_{3,4}$	*H-3*ax $J_{3ax,3eq}$	H-*3*eq $J_{2,3eq}$	*H-4* $J_{4,5}$	*H-5* $J_{5,6endo}$	*H-6*exo $J_{5,6exo}$	*H-6*endo $J_{6exo,6endo}$	*Ph*CH_2	Ph*C*H_2	*Allyl*
7	5.35s	4.81m	4.39dd			3.55dd	4.61dd	3.73dd	4.0dd			4.17dt 5.22dq
	1.5	4.0	6.0			2.0	1.2	5.5	7.5			5.30dq 5.87ddt
8	5.43s	2.94dd	3.21m			3.38dd	4.34dt	3.54dd	3.75dd			4.2dt 5.10dq 5.22dq
	1.5	4.0	4.5			1.0	2.5	7.0	8.0			5.85ddt
9	5.18d	3.36m		1.82m	1.78m	3.20m	4.45m	3.60dd	3.65dd			4.1ddt 5.10dq 5.20dq 5.90ddt
10	5.43s	3.30m		1.82m	1.99m	3.31m	4.60ddd	3.47dd	3.56dd	4.60	7.30m	4.10dt 5.15dq 5.20dq 5.90ddt
11	5.45d	3.34m		1.96m	1.96m	3.63m	4.55m 2.0	3.83dd 4.5	3.78dd 8.0	4.60 AB	7.0m	
12	5.62s 1.5	3.78m 7.0		2.71dd 17.0	2.61 3.5		4.56dd 2.0	3.93dd 4.5	3.85dd 8.0	4.60 AB	7.35m	
13	5.62s 1.5	3.52sd 4.0		5.81ddd 10.0		6.24m 4.5	4.72dt 2.5	3.65m	3.65m	4.9s	7.30m	

TABLE II

^{1}H-N.m.r. data (δ in p.p.m., J in Hz) for **14–47**

Compound	*H-1* $J_{1,2}$	*H-2* $J_{2,3ax}$	*H-3*ax $J_{3ax,3eq}$	*H-3*eq $J_{2,3eq}$	*H-5* $J_{5,6endo}$	*H-6*exo $J_{5,6exo}$	*H-6*endo $J_{6exo,6endo}$	*H-4*^{1} $J_{4^1,4^2}$	*H-4*^{2}	*Ph*CH_2	Ph*CH_2*	*Others*
14	5.42s 1.5	3.52ddd 6.5	1.94dd 15.0	2.52dt 3.5	4.94dd 1.0	3.67dd 5.5	4.37dd 7.5		2.12s	4.60 AB	7.30m	2.0m 3.0m $(CH_2)_3$
15	5.28s 1.5	3.46dt 5.0	1.97dd 15.0	2.18dd 2.5	7.72dd 1.0	3.71dd 5.5	4.41dd 9.0		1.75s	4.50 AB	7.20	1.8m 2.8m $(CH_2)_3$
16	5.23d 1.5	3.50m	2.05m	2.05m	4.20dd 1.2	3.78dd 5.0	4.32dd 8.0		2.68s	4.80 AB	7.30	
17	5.69t 1.5	3.66m 4.0	2.35dd 15.0	1.85ddd 1.0	4.35dd 5.5	3.77dd 9.0	4.17dd		2.30s	4.63 AB	7.35	
18	5.38s 2.0	3.47dt 5.0	1.59dd 15.0	2.33m	4.27dd 1.0	3.72dd 5.5	4.17dd 8.0	4.42q 6.5	1.27d	4.51 AB	7.30m	
19	5.41s 2.0	3.48m 5.0	1.61dd 15.0	1.90m	4.53dd 1.0	3.74dd 5.5	4.19dd 8.0	4.59q 6.5	1.23d	4.53 AB	7.30m	
20	5.45s 2.0	3.48m 4.5	1.61dd 15.0	1.75m	4.65dd 1.0	3.78dd 5.5	3.89ddd 7.5	3.78q 6.5	1.22d	4.53 AB	7.30	
21	5.41s 2.0	3.54m 5.0	1.82dd 15.0	2.07	4.22dd 1.0	3.78dd 6.0	3.96dd 9.0	3.58q 7.5	1.20d	4.60 AB	7.30m	
22	5.39s 2.0	3.51m 5.5	2.19dd 15.0	1.86m	4.41dd 1.0	3.76dd 5.5	4.19dd 8.0	4.1q 7.0	1.59d	4.56 AB	7.35	1.39s 1.37s CMe_2
23	5.36s 2.0	3.47m 6.0	1.85dd 15.0	2.12m	4.33dd 1.0	3.77dd 5.5	4.17dd 8.0	4.41qc 7.0	1.44d	4.54 AB	7.30	1.43s 1.34s CMe_2

24	5.44s 2.0	3.43m 5.0	1.73dd 15.0	1.86m	4.32dd 1.5	3.65dd 5.0	3.72dd 8.0	3.93q 6.5	1.26d	4.62 AB	7.35m	1.45s CMe_2
25	5.43d 2.0	3.43m	1.78m	1.78m	4.41dd 1.5	3.74dd 5.0	3.82dd 8.0	3.84q 7.0	1.23d	4.62 AB	7.35	
26	5.45s 1.5	3.54m 5.0	1.77d 15.0	3.07m	4.28dd 1.5	3.78dd 6.5	4.30dd 8.0	4.47q 6.5	1.39d	4.75 4.56 4.43 AB	7.30m	
27	5.45s 1.0	3.48m 5.0	1.72dd 15.0	1.96m	5.30dd 1.0	3.72dd 7.5	4.18dd 6.5	4.56q	1.36d	3.73 4.56 4.43 AB	7.30m	
28	5.52t 2.0	3.41dt 2.0	1.63dd 15.0	1.98m 6.5	5.16dd 1.5	3.60dd 6.0	3.69dd 8.5	3.51q 6.5	1.32d	4.60 4.62 4.95 AB	7.30m	
29	5.53t 2.0	3.47dt 1.5	1.80dd 15.0	2.50m 5.5	4.46dd 1.0	3.73dd 5.5	4.12dd 8.0	3.61q 6.5	1.29d	4.60 4.70 4.90 AB	7.30m	
30	4.59d 3.5	3.78dd 12.0	2.01dd 15.0	2.10dd 5.0	5.94dd 2.5	3.87dd 8.0	3.99dd 11.5	3.74q 6.5	1.39dd	4.28 4.54 4.59	7.30	3.48 (OMe)
31	4.36d 7.6	3.60ddd 12.0	1.86dd 15.0	2.29dd 5.5	3.90dd 2.5	3.83dd 8.0	3.90dd 11.5	3.69q 6.5	1.31d	4.75 4.65 4.43	7.30	3.63 (OMe)
32	4.82d 3.5	3.74dd 12.0	2.05dd 15.0	2.64dd 5.0	3.85dd 2.5	3.87dd 7.0	3.98 11.5	3.77q 6.5	1.26d	4.60 4.65 4.75	7.30	3.63 (OMe)

(Continued)

TABLE II (continued)

^{1}H-N.m.r. data (δ in p.p.m., J in Hz) for **14–47**

Compound	*H-1* $J_{1,2}$	*H-2* $J_{2,3ax}$	*H-3*ax $J_{3ax,3eq}$	*H-3*eq $J_{2,3eq}$	*H-5* $J_{5,6endo}$	*H-6*exo $J_{5,6exo}$	*H-6*endo $J_{6exo,6endo}$	*H-4*^{1} $J_{4^1,4^2}$	*H-4*^{2}	*PhCH*$_2$	Ph*CH*$_2$	*Others*
33	4.36d	3.50dd	1.74dd	2.58dd	3.70dd	3.77dd	4.01dd	3.71q	1.24d	4.35 4.65	7.30	3.63 (OMe)
	7.5	12.0	15.0	5.0	2.5	7.0	11.5	6.5		4.75		
34	4.75d	3.72ddd	2.02dd	2.45dd	4.10dd	4.36dd	4.50dd	3.70q	1.28d	4.30 4.55	7.30	3.56 (OMe)
	3.5	12.0	15.0	2.5	8.5	12.0	6.5			4.60		2.10 (OAc)
35	4.33d	3.49ddd	1.72dd	2.57dd	3.93dd	4.40dd	4.45dd	3.71	1.26d	4.43 4.65	7.30	3.66 (OMe)
	8.0	12.0	15.0	5.0	2.5	8.0	11.5	6.5		4.70		2.10 (OAc)
36	4.78d	4.08dd	1.79dd	1.89dd	4.06dd	3.68dd	3.96dd	3.81q	1.21d	–	–	3.56 (OMe)
	4.0	12.0	15.0	6.0	3.0	8.5	12.0	6.5				
37	4.30d 8.0	3.70ddd 12.0	1.70dd 15.0	2.03dd 6.0	3.93dd 3.0	3.69dd 9.0	3.94dd 13.0	3.79q 6.5	1.20d	–	–	3.65 (OMe)
38	4.78d 3.5	4.04ddd 12.0	1.71dd 15.0	1.85dd 5.5	3.80dd 3.0	3.62dd 8.0	3.75dd 12.0	3.78q 6.5	1.25d			3.55 (OMe)
39	4.36d 8.0	3.76ddd 12.0	1.64dd 15.0	2.16dd 6.0	3.67dd 3.0	3.90dd 9.0	3.75dd 13.0	3.85q 6.5	1.23d			3.67 (OMe)
40	4.81d	3.80m	2.08m	2.13m	4.24dd	3.56dd	4.03dd	3.64q	1.32d	4.50 4.30	7.30	3.56 (OMe)
	3.5				1.5	11.0	12.0	6.5		4.59		
41	4.6d	3.50m	1.70dd	2.54dd	3.82dd	3.66dd	3.68dd	3.68q	1.22d	4.50 4.60	7.30	3.56 (OMe)
	8.0	11.5	15.0	6.0	3.0	9.5	11.0	6.0		4.75		

42	4.78d	3.70m	1.98dd	2.43dd	4.02	3.60dd	3.60dd	3.68q	1.24d	4.50 4.55	7.30	3.53 (OMe)
	3.5	11.5	15.0	6.0	3.0	10.0	11.0	6.5		4.58		
43	4.34d	3.68m	1.95dd	2.26dd	4.17dd	3.56dd	3.52dd	3.53q	1.25	4.45 4.52	7.30	3.66 (OMe)
	8.0	11.5	15.0	6.0	3.0	9.5	11.0	6.0		4.75		
44	4.78d 3.5	4.09ddd 11.0	1.92dd 13.0	1.88dd 6.5	4.21q 6.5		1.23d	3.82q 6.5	1.28d			3.57 (OMe)
45	4.30dd 8.5	3.68ddd 11.5	1.70dd 13.0	2.09dd 6.0	4.02q 6.5		1.20d	3.77q 6.5	1.23d			3.65 (OMe)
46	4.78d 3.5	4.09ddd 11.0	1.77dd 13.0	1.94dd 6.5	3.95q 6.5		1.16d	3.77q 6.5	1.18d			3.54 (OMe)
47	4.30d 8.5	3.70ddd 11.0	1.63dd 13.0	2.18dd 6.0	3.82q 6.5		1.19d	3.77q 6.5	1.20d			3.66 (OMe)

^{13}C-N.m.r. data (δ in p.p.m.) for **7–19**

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Ph*	*Allyl*	*PhCH$_2$*	PhC*H$_2$*	*C-4^1*	*C-4^2*	*(CH$_2$)$_3$*
7	98.9	75.4	74.2	75.1	74.5	65.5	133.8 129.8 129.1	133.9 117.3 70.3					
8	96.8	47.7	47.5	72.8	75-2	65.3		134.2 117.6 69.8					
9	102.1	66.7	27.7	73.2	73.8	65.1		134.2 116.8 69.3					
10	101.0	72.1	24.9	72.6	74.7	65.6		135.2 116.8 69.9	71.3	127.4–129			
11	100.4	73.7	27.9	67.1	77.6	65.6			71.6	127–129			
12	101.6	75.8	39.4	20.5	79.2	66.8			71.6	127-129			
13	101.3	75.2	31.0	74.8	74.6	64.5			71.6	127–129	62.4	24.1	24.0 26.5 26.2
14	99.0	75.3	28.1	78.3	78.6	67.0			71.6	127–129	55.4	24.8	25.2 27.1 27.4
16	100.3	74.8	32.5	74.1	75.6	65.1			71.9	127–129	213.0	26.5	
17	99.0	73.9	29.4	71.4	77.7	65.6			71.6	127–129	213.0	25.0	
18	100.3	75.2	30.2	71.0	75.9	65.2			69.5	127–129	71.6	16.8	
19	99.8	74.5	29.6	71.7	75.4	64.4			71.8	127–129	71.6	17.2	

TABLE IV

^{13}C-N.m.r. data (δ in p.p.m.) for **20–29**

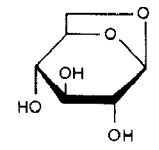
Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-4^1*	*C-4^2*	*PhCH$_2$*	PhCH$_2$	(CH$_3$)$_2$C	(CH$_3$)$_2$C
20	99.9	73.9	29.6	72.8	78.0	65.2	69.6	16.8	71.7	127–128		
21	99.9	74.1	29.3	73.0	78.6	65.4	71.0	17.5	71.7	127–128		
22	99.6	75.1	32.8	78.3	74.4	65.1	80.6	14.7	71.5	127–129	28.0 26.9	106.6
23	100.3	74.6	29.5	79.8	78.0	64.9	79.1	17.6	71.2	127–129	28.0	107.3
24	101.0	72.7	26.7	76.7	79.5	64.7	75.9	16.7	71.2	127–129	29.2	107.0
25	101.1	73.2	30.3	79.6	76.7	65.1	77.9	15.4	71.3	127–129	28.9 27.3	107.3
26	100.8	74.7	26.6	76.0	75.8	65.0	79.0	12.8	62.6 71.6 71.8	127–129		
27	100.2	75.9	30.9	76.6	72.8	64.0	77.9	13.9	64.0 71.5 72.8	127–129		
28	100.7	72.9	29.4	76.1	73.7	64.8	78.9	12.4	62.5 72.0 72.2	127–129		
29	100.5	73.4	25.2	77.6	77.2	65.4	78.4	13.2	62.3 72.3 72.5	127–129		

TABLE V

^{13}C-N.m.r. data (δ in p.p.m.) for **30–47**

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-4^1*	*C-4^2*	*PhCH$_2$*	PhCH$_2$	*OMe*
30	96.9	71.3	27.9	80.1	70.4	60.9	76.2	14.6	61.3 71.2 71.2	127–128	54.9
31	106.5	74.0	32.8	79.6	78.9	61.6	76.1	14.2	65.6 71.3 73.0	127–128	56.7
32	97.5	71.6	25.1	81.4	70.0	61.7	80.1	15.2	71.5 70.9 65.8	127–128	55.3
33	106.8	73.7	31.5	79.8	78.9	61.7	79.8	15.1	65.9 71.3 73.1	127–128	56.8
36	99.7	66.0	32.5	76.5	72.0	61.3	71.3	16.9			56.3
37	107.1	68.0	36.8	76.6	80.0	61.4	71.0	17.4			58.2
38	99.9	65.6	31.3	77.4	72.1	61.8	71.9	18.0			56.3
39	107.2	67.9	36.6	77.5	80.5	61.8	71.6	18.2			58.3
40	97.0	71.5	27.9	80.3	72.1	33.0	75.9	14.0	64.0 71.1 71.6	127–128	55.4
41	106.4	73.0	32.4	80.0	79.8	32.1	76.4	13.1	66.7 71.1 71.6	127–128	56.8

42	97.3	71.6	24.8	80.7	73.0	31.9	80.3	15.7	65.6 70.9 71.6	127–128	55.4
43	106.4	73.1	29.8	80.5	77.6	31.9	79.9	15.2	65.9 71.2 73.1	127–128	56.8
44	99.9	68.0	31.4	76.6	68.1	13.7	71.0	16.7			56.3
45	107.1	68.0	35.8	76.5	76.1	13.9	70.7	17.4			58.3
46	99.9	65.6	31.03	77.4	68.1	13.8	71.9	18.0			56.3
47	107.2	68.0	36.6	77.5	76.2	13.8	71.6	18.2			58.3



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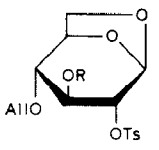
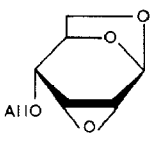


6 R = H
7 R = Ms



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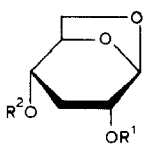
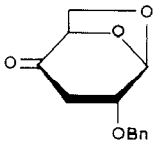


9 R^1 = H, R^2 = All
10 R^1 = Bn , R^2 = All
11 R^1 = Bn , R^2 = H

All = allyl



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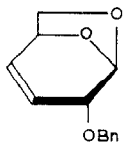


13

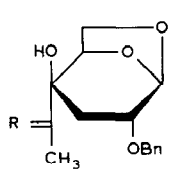
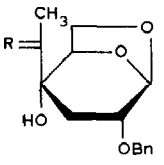
TABLE VI

^{1}H-N.m.r. data (δ in p.p.m.) for yersiniose A and B

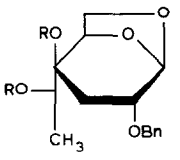
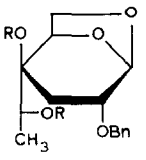
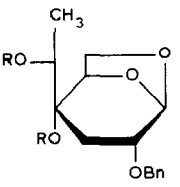
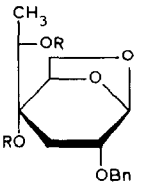
		H-1	*H-2*	*H-3*ax	*H-3*eq	*H-5*	*H-6,6,6*	*H-4'*	*H-4",4",4"*
Yersiniose A	α	4.78	4.09	1.93	1.89	4.21	1.22	3.82	1.28
	β	4.30	3.70	1.70	2.09	4.03	1.22	3.76	1.23
Yersiniose B	α	4.78	4.09	1.77	1.95	3.95	1.16	3.77	1.19
	β	4.30	3.69	1.63	2.18	3.82	1.18	3.77	1.20

removed[9] by the action of $PdCl_2$. Oxidation[10] of the resulting alcohol **11** then afforded the ketone **12** in good yield. Treatment of **12** with 2-lithio-2-methyl-1,3-dithiane[4] afforded the derivatives **14** and **15** in the ratio 1:1.6, which were isolated by chromatography on silica gel. The structures of **14** and **15** were confirmed by the ^{1}H- and ^{13}C-n.m.r. data and n.O.e. experiments. For example, pre-irradiation of the CH_3 group increased the intensity of the signal for H-5 in **14** and for H-6*endo* in **15**, which indicated the side chain to be axial in **14** and equatorial in **15**.

Treatment[4] of **14** or **15** with $HgCl_2$ in the presence of $CdCO_3$ gave the ketone **16** or **17** in good yield. The structures of **16** and **17** were confirmed by the ^{1}H- and ^{13}C-n.m.r. data. The most significant differences were the chemical shifts and multiplicity of the signals for **16** and **17** for H-1 (d at 5.53 and t at 5.69 p.p.m.), H-3*ax* (m at 2.05 and at 2.35 p.p.m.), H-3*eq* (m at 2.05 and dd at 1.85 p.p.m.), and H-5 (d at 4.22 and dd at 4.35 p.p.m.). In the ^{13}C-n.m.r. spectra, the differences were not so significant, although the chemical shifts of the respective signals for C-3 (32.5 and 29.4 p.p.m.) and C-4 (74.1 and 71.8 p.p.m.) were diagnostic. The above spectra make it easy to distinguish between **16** and **17**.

14 R= $-SCH_2CH_2CH_2S-$ 15 R = $-SCH_2CH_2CH_2S-$
16 R=O 17 R = O

18 R = H 19 R = H 20 R = H 21 R = H
22 R,R= $Me_2C=$ 23 R,R= $Me_2C=$ 24 R,R= $Me_2C=$ 25 R,R= $Me_2C=$
26 R = Bn 27 R = Bn 28 R = Bn 29 R = Bn

Reduction of **16** or **17** with sodium borohydride in ethanol afforded two pairs of alcohols **18–19** and **20–21**, respectively, isomeric at C-4^1, which were isolated by chromatography on silica gel[4]. The combined yield of **18** and **19** was 82%, with the ratio 2:1. The other pair of alcohols was formed in quantitative yield and in the ratio ~ 1:1.

The absolute configuration of the new chiral centre (C-4^1) in **18–21** was determined by n.O.e. experiments for the isopropylidene derivatives **22–25**, which were obtained in good yield after reaction with 2,2-dimethoxypropane in the presence of toluene-*p*-sulfonic acid. On pre-irradiation of the CH_3 group (C-4^2), only the intensities of the signals of H-3*eq* (2%) in **23**, H-5 (2%) in **22**, H-3*ax* (2.5%) and H-6*endo* (1%) in **24** increased, which indicated the proximity of the CH_3 group and the above protons and determined the absolute configuration at C-4^1. The configuration at C-4^1 in **25** and hence in **21** should be the reverse of that of **24**. Thus, the pairs of alditols **19**,**20** and **18**,**21** had the D- and L-*glycero* configuration of their side chains, respectively.

The next stage of the transformation of the diols **18** and **19** into the target compounds involved methanolysis and then deoxygenation of the primary hydroxymethyl groups in the resulting glycosides. Both HO-4 and HO-4^1 were benzylated in order to avoid exchange of the side chain with the cyclic C-5,6 fragment or formation of methyl α- and β-glucofuranosides. The benzyl ethers **26–29** were obtained in good yields and their structures were confirmed by the n.m.r. data.

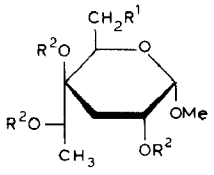
In studying the cleavage of the 1,6-anhydro ring, a necessary step in the formation of the target compounds, it was found that selective cleavage occurred on acetolysis (0.2% of H_2SO_4 in Ac_2O), and methanolysis of the products then gave the methyl glycosides **30–33**.

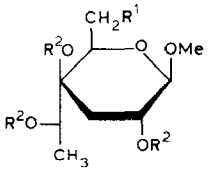
The homogeneous methyl glycosides **30** and **31** were isolated easily, but **32** and **33** could be isolated only as the acetates **34** and **35**. The benzyl groups were removed easily by catalytic hydrogenolysis[11] to give the branched 3-deoxy derivatives **36–39**.

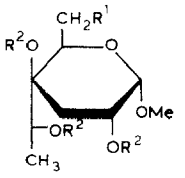
The approach to the target compounds then involved the transformation of **30–33** into the bromides **40–43**. The methyl α- and β-yersiniosides **44–47** with known configuration at C-4[1] were obtained in good yields from **40–43** by catalytic hydrogenation.

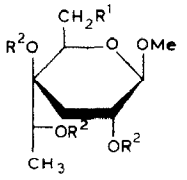
Comparison (See Tables) of the ^{1}H-n.m.r. data for (natural) methyl α- and β-yersiniosides A and B with those of the synthetic compounds **44–47** established the L- and D-*glycero* configuration, respectively, in the side chains.

The ^{1}H-n.m.r. spectra (Table VI) were characteristic, since the signals for H-3*ax*,3*eq* were sensitive to a change in the configuration of the side chain. Thus, for the α anomers, the signals of H-3*ax* and H-3*eq* were at 1.92 and 1.88 p.p.m. for yersiniose A, and 1.77 and 1.95 p.p.m. for yersiniose B; for the β anomers, these signals were at 1.70 and 2.09 p.p.m. for yersiniose A, and 1.57 and 2.12 p.p.m. for yersiniose B. These differences may serve generally to determine the configuration of the side chain in this kind of sugar.









30 R^1 = OH, R^2 = Bn	**31** R^1 = OH, R^2 = Bn	**32** R^1 = OH, R^2 = Bn	**33** R^1 = OH, R^2 = Bn
		34 R^1 = OAc, R^2 = Bn	**35** R^1 = OAc, R^2 = Bn
36 R^1 = OH, R^2 = H	**37** R^1 = OH, R^2 = H	**38** R^1 = OH, R^2 = H	**39** R^1 = OH, R^2 = H
40 R^1 = Br, R^2 = Bn	**41** R^1 = Br, R^2 = Bn	**42** R^1 = Br, R^2 = Bn	**43** R^1 = Br, R^2 = Bn
44 R^1 = R^2 = H	**45** R^1 = R^2 = H	**46** R^1 = R^2 = H	**47** R^1 = R^2 = H

EXPERIMENTAL

The ^{1}H and ^{13}C-n.m.r. spectra were recorded with a Bruker WM-250 spectrometer for solutions in $CDCl_3$ and D_2O (internal Me_4Si and MeOH, respectively) and the data are recorded in Tables I–VI. Optical rotations for solutions in $CHCl_3$ and H_2O were determined with a Perkin–Elmer 141 M polarimeter at 20°. T.l.c. was performed on Silica Gel 60 (Merck) with detection by charring with sulfuric acid. Column chromatography was performed on silica gel L (60–100 mesh, Č.S.S.R.).

4-O-Allyl-1,6-anhydro-3-O-methanesulfonyl-2-O-p-toluenesulfonyl-β-D-glucopyranose (**7**). — To a solution of **6**[5] (2.1 g, 0.06 mol) in dry dichloromethane (200 mL) was added triethylamine (12.5 mL, 0.09 mol), and the mixture was cooled to −15°. Methanesulfonyl chloride (5.42 mL, 0.07 mol) was added with stirring. After 20 min, the

mixture was washed successively with water, M H_2SO_4, saturated aqueous sodium hydrogencarbonate, and water, dried ($CaCl_2$), and concentrated to dryness. Crystallisation of the residue from ethanol gave **7** (18.9 g 75%), m.p. 134°, $[\alpha]_D$ −26° (*c* 0.6).

Anal. Calc. for $C_{17}H_{21}O_9S_2$ (433.68): C, 47.08; H, 4.88; S, 14.79. Found C, 47.10; H, 4.90; S, 14.77.

*4-O-Allyl-1,6:2.4-dianhydro-*D*-allopyranose* (**8**). — To a solution of **7** (18.4 g, 44 mmol) in 1:1 dichloromethane–methanol (140 mL) at 0° was added methanolic 2M sodium methoxide (70 mL, 0.14 mol). The mixture was stirred at 20° until the reaction was complete (20 h), then diluted with water (200 mL). The upper layer was extracted with chloroform (2 × 160 mL), and the organic phase and extracts were combined, washed with saturated saline, dried (Na_2SO_4), and concentrated to give **8** (7.3 g, 90%) as a syrup, $[\alpha]_D$ +80° (*c* 0.5).

Anal. Calc. for $C_9H_{12}O_4$ (184.20): C, 58.69; H, 6.57. Found: C, 58.73; H, 6.60.

*4-O-Allyl-1,6-anhydro-3-deoxy-β-*D-ribo-*hexopyranose* (**9**). — To a solution of **8** (12.0 g, 0.065 mol) in dry ether (200 mL) was added portionwise lithium aluminium hydride (2.2 g, 0.59 mol), and the mixture was boiled under reflux for 2 h. Excess of the reagent was decomposed by the addition of water (25 mL), the mixture was washed with aqueous 10% potassium hydroxide (10 mL) and filtered through a bed of alumina which was then washed with ether, and the combined filtrate and washings were concentrated. The residue was dried *in vacuo* to give **9** (12 g, 95%) as a syrup, $[\alpha]_D$ −59° (*c* 0.8).

Anal. Calc. for $C_9H_{14}O_4$ (186.21): C, 58.05; H, 7.57. Found: C, 58.10, H, 7.59.

*4-O-Allyl-1,6-anhydro-2-*O*-benzyl-3-deoxy-*D-ribo-*hexopyranose* (**10**). — To a solution of **9** (12 g, 0.065 mol) in methyl sulfoxide (100 mL) was added 1.4M sodium methylsulfinylmethanide in methyl sulfoxide (50 mL, 0.07 mol). The mixture was stirred for 0.5 h, then benzyl chloride (10.3 mL, 0.07 mol) was added dropwise with cooling. After 1 h, the mixture was diluted with water and extracted with chloroform (thrice), and the combined extracts were washed with water and saturated saline, and concentrated. Chromatography (benzene–ether gradient) of the residue gave **10** (16.5 g, 94%), isolated as a syrup, $[\alpha]_D$ −67° (*c* 0.7).

Anal. Calc. for $C_{16}H_{20}O_4$ (276.34): C, 69.54; H, 7.29. Found: C, 69.61; H, 7.31.

*1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-*D-erythro-*hex-3-enopyranose* (**13**). — To a solution of **10** (3 g, 10.5 mmol) in dry methyl sulfoxide (20 mL) was added potassium *tert*-butoxide (1.2 g, 10.7 mmol). The mixture was kept for 2 h at 30°, then poured into water, and the product was extracted with ether (3 × 50 mL). The combined extracts were washed with saline, then concentrated. Chromatography (chloroform) of the residue gave **13** (1.90 g, 87%), isolated as a syrup, $[\alpha]_D$ −98° (*c* 0.6).

Anal. Calc. for $C_{13}H_{14}O_3$ (218.25): C, 17.54; H, 6.48. Found: C, 17.52; H, 6.51.

*1,6-Anhydro-2-*O*-benzyl-3-deoxy-β-*D-ribo-*hexopyranose* (**11**). — To a solution of **10** (9 g, 32.6 mmol) in 20:1 acetic acid–water (50 mL) were added $PdCl_2$ (8.2 g, 46 mmol) and sodium acetate (16 g). The mixture was stirred at ambient temperature, allyl alcohol (10 mL) was added, and the mixture was filtered through a bed of silica gel and concentrated. Column chromatography (benzene–ether gradient) of the residue gave **11** (6.2 g, 80%), isolated as a syrup, $[\alpha]_D$ −26° (*c* 0.5).

Anal. Calc. for $C_{13}H_{16}O_4$ (236.27): C, 66.08; H, 6.83. Found: C, 66.09; H, 6.81.

*1,6-Anhydro-2-O-benzyl-3-deoxy-*D-erythro-*hexopyranos-4-ulose* (**12**). — To a solution of oxalyl chloride (4.55 mL, 0.052 mol) in dichloromethane (50 mL) at −65° was added dropwise a solution of methyl sulfoxide (7.4 mL, 0.052 mol) in dichloromethane (30 mL) during 10 min and, after a further 5 min, a solution of **11** (6 g, 0.03 mol) in dichloromethane (50 mL). The mixture was kept at −65° for 15 min, then treated dropwise with triethylamine (26 mL, 0.2 mol), diluted with chloroform (200 mL), washed with saline, and concentrated. Chromatography (benzene–ether gradient) of the residue afforded **12** (5.5 g, 90.4%), isolated as a syrup, $[\alpha]_D$ −50.5° (*c* 0.5).

Anal. Calc. for $C_{13}H_{14}O_4$ (234.25): C, 66.65; H, 6.04. Found: C, 66.68; H, 6.09.

*1,6-Anhydro-2-O-benzyl-3-deoxy-4-C-(2-methyl-1,3-dithian-2-yl)-β-*D-xylo- (**14**) and *-β-*D-ribo-*hexopyranose* (**15**). — To a solution of 2-methyl-1,3-dithiane (18 mL, 130 mmol) in dry oxolane (100 mL) was added a solution of butyl-lithium in hexane (21.8 mL, 28.4 mmol). The mixture was stirred for 2.5 h, then cooled to −70°, and a solution of **12** (6.05 g, 26 mmol) in oxolane (50 mL) was added dropwise. After 3 h, acetic acid (6 mL) was added and the mixture was concentrated. Chromatography of the residue (benzene–ether gradient) gave **14** (57.7%), R_F 0.5 (benzene–ethyl acetate, 3:1), isolated as a syrup, $[\alpha]_D$ −42° (*c* 0.6), and **15** (3.68 g, 38.5%), R_F 0.55, isolated as a syrup, $[\alpha]_D$ −32° (*c* 0.7). N.O.e. effects: **14** [CH_3]H-5, 2.5%; **15** [CH_3]H-6*endo*, 3%.

Anal. Calc. for $C_{18}H_{24}O_4S_2$ (368.52): C, 58.67; H, 6.56; S, 17.40. Found (for **14**): C, 58.70; H, 6.60; S, 17.42. Found (for **15**): C, 58.65; H, 6.58; S, 17.41.

*4-C-Acetyl-1,6-anhydro-2-O-benzyl-3-deoxy-β-*D-xylo-*hexopyranose* (**16**). — A mixture of **14** (1.62 g, 4.4 mmol), mercuric chloride (3.6 g, 13.2 mmol), and cadmium carbonate (4.6 g, 26.4 mmol) in 10:1 acetone–water (30 mL) was heated under reflux for 8 h, then filtered, and concentrated. Chromatography (benzene–ethyl acetate) of the residue gave **16** (1.1 g, 91%), isolated as a syrup, $[\alpha]_D$ −50° (*c* 0.5).

Anal. Calc. for $C_{15}H_{14}O_5$ (278.31): C, 64.74; H, 6.52. Found: C, 64.75; H, 6.50.

*4-C-Acetyl-1,6-anhydro-2-O-benzyl-3-deoxy-β-*D-ribo-*hexopyranose* (**17**). — Prepared from **15** as described above, **17** (85%) had $[\alpha]_D$ −29.5° (*c* 0.5).

Anal. Calc. for $C_{15}H_{14}O_5$ (278.31): C, 64.74; H, 6.52. Found: C, 64.76; H, 6.51.

*1,6-Anhydro-2-O-benzyl-3-deoxy-4-C-(*L-glycero- and D-glycero-4^1-*hydroxyethyl)-β-*D-xylo-*hexopyranose* (**18** and **19**). — A solution of **16** (0.35 g, 1.3 mmol) in methanol (5 mL) was stirred with sodium borohydride (0.34 g, 10 mmol) for 30 min, then treated with KU-2 (H^+), resin, filtered, and concentrated. Methanol was distilled several times from the residue, and chromatography (100:3 dichloromethane–methanol) then gave **18** (0.1 g, 27.3%), isolated as a syrup, R_F 0.55, $[\alpha]_D$ −11° (*c* 0.8); and **19** (0.2 g, 54.6%), R_F 0.5, $[\alpha]_D$ −30° (*c* 0.5).

Anal. Calc. for $C_{15}H_{20}O_5$ (280.33): C, 64.27; H, 7.19. Found (for **18**): C, 64.30; H, 7.19. Found (for **19**): C, 64.28; H, 7.18.

*1,6-Anhydro-2-O-benzyl-3-deoxy-4-C-(*D-glycero- *and* L-glycero-4^1-*hydroxyethyl)-β-*D-ribo-*hexopyranose* (**20** *and* **21**). – Prepared from compound **17** as described above, syrupy **20** (55%) had R_F 0.6, $[\alpha]_D$ −47° (*c* 0.7), and syrupy **21** (45%) had R_F 0.65, $[\alpha]_D$ −42° (*c* 0.8).

Anal. Calc. for $C_{15}H_{20}O_5$ (280.33): C, 64.27; H, 7.19. Found (for **20**): C, 64.29; H, 7.21. Found (for **21**): C, 64.25; H, 7.19.

*1,6-Anhydro-2-*O*-benzyl-3-deoxy-4-*C*-(*D*-glycero-4^1-hydroxyethyl)-4,4^1-*O*-isopropylidene-β-*D*-xylo-hexopyranose* (**23**). — To a solution of **19** (0.28 g, 1 mmol) in acetone (5 mL) were added 2,2-dimethoxypropane (1 mL) and *p*-toluenesulfonic acid monohydrate (0.1 g). The mixture was stirred for 30 min, neutralised with sodium carbonate, and concentrated. Chromatography (benzene–ethyl gradient) of the residue gave **23** isolated as a syrup (0.3 g, 94%), $[\alpha]_D$ −51° (*c* 0.7). N.O.e. effect: $[CH_3]$H-3*eq* (2%).

Anal. Calc. for $C_{18}H_{24}O_5$ (320.29) C, 67.48; H, 7.55. Found C, 67.47; H, 7.57.

This procedure was employed to prepare the following compounds.

1,6-Anhydro-2-*O*-benzyl-3-deoxy-4-*C*-(*L*-*glycero*-4^1-hydroxyethyl)-4,4^1-*O*-isopropylidene-β-*D*-*xylo*-hexopyranose (**22**, 90%), prepared from **18**, had $[\alpha]_D$ −31° (*c* 0.6). N.O.e. effect: $[CH_3]$H-5 (2.0%).

Anal. Found: C, 67.49; H, 7.54.

1,6-Anhydro-2-*O*-benzyl-3-deoxy-4-*C*-(*D*-*glycero*-4^1-hydroxyethyl)-4,4^1-*O*-isopropylidene-β-*D*-*ribo*-hexopyranose (**24**, 95%), prepared from **20**, had $[\alpha]_D$ −35° (*c* 0.5). N.O.e. effect: $[CH_3]$H-6*endo* (1.0%).

Anal. Found: C, 67.50, H, 7.56.

Deacetonation of **23**. — A solution of **23** (0.255 g, 0.78 mmol) in methanol (5 mL) was stirred with KU-2 (H^+) resin for 20 min, then filtered. The resin was washed with methanol, and the filtrate and washings were combined and concentrated to give **19** (0.2 g, 89.6%), $[\alpha]_D$ −30° (*c* 0.5).

*1,6-Anhydro-2,4,4^1-tri-*O*-benzyl-3-deoxy-4-*C*-(*D*-glycero-4^1-hydroxyethyl)-β-*D*-xylo-hexopyranose* (**27**). — To a solution of **19** (0.3 g, 1.08 mmol) in *N,N*-dimethylformamide (5 mL) was added sodium hydride (0.5 g), and the mixture was stirred for 40 min. Benzyl chloride (0.4 mL, 1.3 mmol) was added with cooling and stirring was continued for 1 h. The mixture was then diluted with ice–water, the product was extracted with chloroform, and the extract was washed with saline and concentrated. Chromatography (benzene–ether gradient) of the residue gave **27** (0.35 g, 78%), isolated as a syrup, $[\alpha]_D$ −80° (*c* 0.5).

Anal. Calc. for $C_{29}H_{32}O_5$ (460.58): C, 75.63; H, 7.00. Found: C, 75.66; H, 6.99.

The following compounds were prepared in a similar manner.

1,6-Anhydro-2,4,4^1-tri-*O*-benzyl-3-deoxy-4-*C*-(*L*-*glycero*-4^1-hydroxyethyl)-β-*D*-*xylo*-hexopyranose (**26**, 60%), syrup, prepared from **18**, had $]\alpha]_D$ −33° (*c* 0.7).

Anal. Found: C, 75.62; H, 7.02.

1,6-Anhydro-2,4,4^1-tri-*O*-benzyl-3-deoxy-4-*C*-(*D*-*glycero*-4^1-hydroxyethyl)-β-*D*-*ribo*-hexopyranose (**28**, 90%), syrup, prepared from **20**, had $[\alpha]_D$ −34° (*c* 0.6).

Anal. Found: C, 75.65; H, 6.98.

1,6-Anhydro-2,4,4^1-tri-*O*-benzyl-3-deoxy-4-*C*-(*L*-*glycero*-4^1-hydroxyethyl)-β-*D*-*ribo*-hexopyranose (**29**, 91%), syrup, prepared from **21**, had $[\alpha]_D$ −28° (*c* 0.8).

Anal. Found: C, 75.64; H, 7.03.

*Methyl 2,4,4^1-tri-*O*-benzyl-3-deoxy-4-*C*-(*L*-glycero-4^1-hydroxyethyl)-α-* (**30**) *and*

-*β*-D-xylo-*hexopyranoside* (**31**). — To a solution of **26** (0.33 g, 0.8 mmol) in acetic anhydride (12.5 mL) at 0° was added conc. sulfuric acid (0.3 mL). The mixture was stirred for 4 min, then diluted with ice–water, stirred for 2 h, neutralised with sodium hydrogencarbonate, and extracted with chloroform (3 × 50 mL). The combined extracts were washed with water and saline, then concentrated. A solution of the residue in methanolic 1% hydrogen chloride (10 mL) was boiled under reflux for 2 h, then concentrated. Chromatography (benzene–ether) of the residue gave **30** (51 mg, 15%), isolated as a syrup, R_F 0.5 (benzene–ether, 3:1), $[\alpha]_D$ +49° (*c* 1.0); and **31** (15%), isolated as a syrup, R_F 0.55, $[\alpha]_D$ +17° (*c* 0.5).

Anal. Calc. for $C_{30}H_{36}O_6$ (492.62): C, 73.15; H, 7.37. Found (for **30**): C, 73.20; H 7.39. Found (for **31**): C, 73.18; H, 7.40.

Methyl 2,4,4'-tri-O-*benzyl-3-deoxy-4*-C-(D-glycero-*4'-hydroxyethyl*)-α- (**32**) *and* -*β*-D-xylo-*hexopyranoside* (**33**). — Prepared (60% combined yield) from **27**, as described above, the mixture (0.2 g) of **32** and **33** was dissolved in dry pyridine (25 mL) and acetic anhydride (20 mL) was added. After storage for 3 h at 20°, the mixture was concentrated. Chromatography (benzene–ether gradient) of the residue gave the syrupy acetates **34** (77 mg 34%), R_F 0.5, $[\alpha]_D$ +12° (*c* 0.4), and **35** (105 mg, 46%), R_F 0.55, $[\alpha]_D$ −3.6° (*c* 0.6).

To a solution of **34** (77 mg, 0.14 mmol) in dry methanol (30 mL) was added triethylamine (0.4 mL, 0.3 mmol), and the mixture was heated for 1 h at 60°, then concentrated to give **32** (67 mg, 97%), $[\alpha]_D$ +8.2° (*c* 0.5).

Anal. Calc. for $C_{30}H_{36}O_6$ (492.62): C, 73.15; H, 7.37. Found: C, 73.13; H, 7.39.

Likewise, **35** afforded **33** (98%), $[\alpha]_D$ −6.1° (*c* 0.3).

Anal. Found: C, 73.13; H, 7.38.

Methyl 3-*deoxy-4*-C-(L-glycero-*4'-hydroxyethyl*)-α-D-xylo-*hexopyranoside* (**36**). — A solution of **30** (25 mg, 0.05 mmol) in methanol (3 mL) was hydrogenolysed over 50 mg of 10% Pd/C for 3 h at ~ 1 atm. of hydrogen, then filtered, and concentrated. Chromatography (chloroform–methanol) of the residue gave **36** (10 mg, 90%), isolated as a syrup, $[\alpha]_D$ +76° (*c* 0.1, water).

Anal. Calc. for $C_9H_{18}O_6$ (222.24): C, 48.64; H, 8.16. Found: C, 48.62; H, 8.14.

The following compounds were prepared in a similar manner.

Methyl 3-deoxy-4-*C*-(L-*glycero*-4'-hydroxyethyl)-*β*-D-*xylo*-hexopyranoside (**37**, 90%), prepared from **31**, was a syrup with $[\alpha]_D$ −26° (*c* 0.1, water).

Anal. Found: C, 48.60; H, 8.18.

Methyl 3-deoxy-4-*C*-(D-*glycero*-4'-hydroxyethyl)-α-D-*xylo*-hexopyranoside (**38**, 90%), prepared from **32**, was a syrup with $[\alpha]_D$ +110° (*c* 0.1, water).

Anal. Found: C, 48.63; H, 8.15.

Methyl 3-deoxy-4-*C*-(D-*glycero*-4'-hydroxyethyl)-*β*-D-*xylo*-hexopyranoside (**39**, 90%), prepared from **33**, was a syrup with $[\alpha]_D$ −53° (*c* 0.1, water).

Anal. Found: C, 48.66; H, 8.19.

Methyl2,4,4'-tri-O-*benzyl-6-bromo-3,6-dideoxy-4*-C-(L-glycero-*4'-hydroxyethyl*)-α-D-xylo-*hexopyranoside* (**40**). — To a solution of **30** (40 mg, 0.07 mmol) in pyridine (2 mL) were added trimethylphosphine (50 mg, 0.22 mmol) and carbon tetrabromide (60 mg, 0.2 mmol). The mixture was heated for 3 h at 60°, then methanol

(0.2 mL) and M HCl (5 mL) were added, and the product was extracted with ether. The extract was washed with water and saline, dried (Na_2SO_4), and concentrated. Chromatography (benzene–ether) of the residue gave **40** (36 mg, 80%), isolated as a syrup, $[\alpha]_D$ +85° (*c* 0.2).

Anal. Calc. for $C_{30}H_{35}BrO_5$ (555.53): C, 64.86; H, 6.35. Found: C, 64.88; H, 6.32.

The following compounds were prepared in an analogous manner and isolated as syrups.

Methyl-2,4,4^1-tri-*O*-benzyl-6-bromo-3,6-dideoxy-4-*C*-(L-*glycero*-4^1-hydroxyethyl)-β-D-*xylo*-hexopyranoside (**41**, 82%), prepared from **31**, had $[\alpha]_D$ +34° (*c* 0.1).

Anal. Found: C, 64.87; H, 6.35.

Methyl 2,4,4^1-tri-*O*-benzyl-6-bromo-3,6-dideoxy-4-*C*-(D-*glycero*-4^1-hydroxyethyl)-α-D-*xylo*-hexopyranoside (**42**, 82%), prepared from **32**, had $[\alpha]_D$ +27° (*c* 0.2).

Anal. Found: C, 64.89; H, 6.37.

Methyl 2,4,4^1-tri-*O*-benzyl-6-bromo-3,6-dideoxy-4-*C*-(D-*glycero*-4^1-hydroxyethyl))-β-D-*xylo*-hexopyranoside (**43**, 83%), prepared from **33**, had $[\alpha]_D$ +17° (*c* 0.2).

Anal. Found. C, 64.84; H, 6.33.

Methyl 3,6-dideoxy-4-C-(L-glycero-*4^1-hydroxyethyl)*-α-D-xylo-*hexopyranoside* (**44**). — A solution of **40** (50 mg, 0.12 mmol) in methanol (155 mL) was hydrogenolysed at elevated pressure in the presence of 10% Pd/C (60 mg). The reaction was monitored by t.l.c. The mixture was filtered and concentrated. Chromatography (dichloromethane–methanol, 10:1) of the residue gave **44** (15 mg, 70%), isolated as a syrup, $[\alpha]_D$ +77° (*c* 0.1, water).

Anal. Calc. for $C_9H_{18}O_5$ (206.24): C, 52.41; H, 8.79. Found: C, 52.40; H, 8.78.

The following compounds were prepared in an analogous manner.

Methyl 3,6-dideoxy-4-*C*-(L-*glycero*-4^1-hydroxyethyl)-β-D-*xylo*-hexopyranoside (**45**, 74%), prepared from **41**, was a syrup, $[\alpha]_D$ −53° (*c* 0.1, water).

Anal. Found: C, 52.43; H, 8.77.

Methyl 3,6-dideoxy-4-*C*-(D-*glycero*-4^1-hydroxyethyl)-α-D-*xylo*-hexopyranoside (**46**, 68%), prepared from **42**, was a syrup, $[\alpha]_D$ +123° (*c* 0.5, water).

Anal. Found C, 52.45; H, 8.81.

Methyl 3,6-dideoxy-4-*C*-(D-*glycero*-4^1-hydroxyethyl)-β-D-*xylo*-hexopyranoside (**47**, 69%), prepared from **43**, was a syrup, $[\alpha]_D$ −59° (*c* 0.2, water).

Anal. Found: C, 52.39; H, 8.82.

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