Carbohydrate Research, 100 (1982) 177–193
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

SEQUENTIAL SYNTHESIS AND ^{13}C-N.M.R. SPECTRA OF METHYL β-GLYCOSIDES OF (1→4)-β-D-XYLO-OLIGOSACCHARIDES*†

PAVOL KOVÁČ‡ AND JÁN HIRSCH
Institute of Chemistry, Slovak Academy of Sciences, 809 33 Bratislava (Czechoslovakia)
(Received June 9th, 1981; accepted for publication, July 6th, 1981)

ABSTRACT

The reaction of 2,3-di-*O*-acetyl-4-*O*-benzyl-α,β-D-xylopyranosyl bromide (**2**) with methyl 2,3-di-*O*-acetyl-β-D-xylopyranoside gave methyl *O*-(2,3-di-*O*-acetyl-4-*O*-benzyl-β-D-xylopyranosyl)-(1→4)-2,3-di-*O*-acetyl-β-D-xylopyranoside (**22**). Catalytic hydrogenolysis of **22** exposed HO-4′ which was then condensed with **2**. This sequence of reactions was repeated three more times to afford, after complete removal of protecting groups, a homologous series of methyl β-glycosides of (1→4)-β-D-xylo-oligosaccharides. ^{13}C-N.m.r. spectra of the synthetic methyl β-glycosides (di- to hexa-saccharide) are presented together with data for six other, variously substituted, homologous series of (1→4)-D-xylo-oligosaccharides.

INTRODUCTION

Glycosides of oligosaccharides where the aglycon simulates the polysaccharide backbone are important model compounds in studies of natural polymers. A feature characteristic of hardwood xylans is a β-D-xylopyranosyl group, or a short-chain (1→4)-β-D-xylo-oligosaccharide (xylodextrin) attached mostly at O-3 of certain D-xylosyl residues that form the main β-(1→4)-linked polysaccharide backbone[3]. We have described syntheses of methyl β-glycosides of positionally isomeric D-xylobioses[4,5] and D-xylotrioses[1,6–8], as models representing the sites of branching in xylan-type polysaccharides, and we now report syntheses of methyl β-glycosides of a homologous series of linear (1→4)-β-D-xylo-oligosaccharides by stepwise construction of the oligosaccharide chain (sequential synthesis).

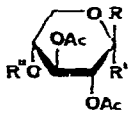
RESULTS AND DISCUSSION

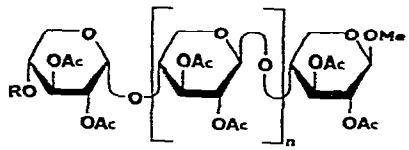
Synthesis. — In the present synthesis of methyl β-glycosides of (1→4)-β-D-xylo-oligosaccharides, 2,3-di-*O*-acetyl-4-*O*-benzyl-α,β-D-xylopyranosyl bromide (**2**) and methyl 2,3-di-*O*-acetyl-β-D-xylopyranoside[9] (**3**) were used as the glycosylating

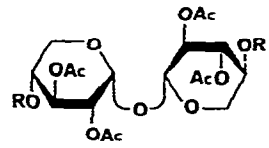
*Alternative Syntheses of Methylated Sugars, Part XXIV. For Part XXIII, see ref. 1.
†For a preliminary account of part of this work, see ref. 2.
‡Present address: BACHEM, Inc., 3132 Kashiwa Str., Torrance, CA 90505, U.S.A.

0008-6215/82/0000–0000/S 02.75,

agent and initial nucleophile, respectively. Our strategy for the stepwise construction of xylodextrins was based on the idea that the reaction of **2** with **3** would give a disaccharide derivative in which HO-4′ could be selectively exposed by catalytic hydrogenolysis and made available for another condensation with the same glycosyl halide.







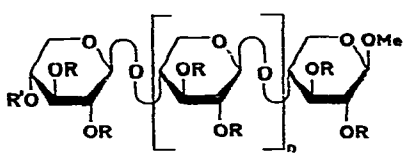
	R	R′	R″
1	OAc	H	Bzl
2	H,Br		Bzl
3	OMe	H	H
4	H	OH	Bzl

	n	R	Series
7	0	Bzl	A
8	1	Bzl	A
9	2	Bzl	A
10	3	Bzl	A
11	4	Bzl	A
12	0	H	B
13	1	H	B
14	2	H	B
15	3	H	B
16	4	H	B
17	0	Ac	C
18	1	Ac	C
19	2	Ac	C
20	3	Ac	C
21	4	Ac	C

5 R=Bzl
6 R=Ac

Compound **2**, obtained by treatment of 1,2,3-tri-*O*-acetyl-4-*O*-benzyl-β-D-xylopyranose[10] (**1**) with hydrogen bromide in dichloromethane, is very reactive. It partially decomposes during t.l.c. but, when freshly prepared, it reacts with sugar nucleophiles to yield the expected oligosaccharides. Since the condensation of **2** with **3** is the key step in the present approach, this reaction was studied in detail (preliminary experiments, not reported). The condensations were performed at ambient temperature (*a*) in acetonitrile, in the presence of mercuric cyanide; (*b*) in chloroform, in the presence of silver carbonate; (*c*) in chloroform, in the presence of mercuric cyanide and mercuric bromide; and (*d*) in toluene, in the presence of mercuric cyanide and mercuric bromide. Reactions (*b*) and (*c*) did not give satisfactory yields of the desired products. High conversion of **3** was observed under conditions (*a*) and (*d*), but whereas the disaccharides **22** and **7** were formed in the ratio of ~2:1 under the former conditions, the stereoselectivity of the reaction in toluene was unfavourable for the preparation of β-linked (1→4)-xylo-oligosaccharides. The oligosaccharide-yielding condensations of nucleophiles **3** and **27–30** with **2** were carried out under the optimum conditions, *i.e.*, in acetonitrile with mercuric cyanide as the catalyst and hydrogen bromide scavenger. The stereochemistry was independent of the chain-length of the nucleophile. A 2–2.5-fold excess of **2** was used in the reac-

tions involving **3**, **27**, and **28**; for the preparation of the penta- and hexa-saccharides, 3 equivalents of **2** were used. These large excesses of **2** were necessary to compensate for losses due to side reactions, and caused the nucleophiles to react almost completely. The condensation products were isolated by gradient elution from columns of silica gel. Except for the α-linked disaccharide derivative **7**, eluted from the column together with the non-reducing disaccharide **5** (a reaction by-product), the desired oligosaccharides were well separated from the products of side reactions. The configuration at the newly formed inter-sugar linkage in the pairs of α- and β-linked oligosaccharides **7** and **22**, **8** and **23**, **9** and **24**, **10** and **25**, and **11** and **26** was tentatively assigned on the basis of specific optical rotation, and confirmed by ^{13}C-n.m.r. spectroscopy (see below). In addition to oligosaccharides **7–11** and **22–26**, all the reaction mixtures of condensation reactions contained (t.l.c.) **4** (the product of hydrolysis of **2**) and the non-reducing disaccharide derivative **5** (the product of the reaction of **2** and **4**). The structures of **4** and **5** (isolated during the preparation of **22**) were fully established by ^{13}C-n.m.r. spectroscopy, and by conversion into the known[11] compound **6**, respectively. Oligosaccharides **7–11** showed higher chromatographic mobilities than their β-linked counterparts **22–26**. The difference in R_F values for pairs of α- and β-linked compounds diminished with increasing chain-length of oligosaccharides and, starting with tetrasaccharides, multiple development of chromatograms was necessary to achieve satisfactory resolution. Therefore, the yields of pure substances depended critically upon the efficiency of chromatographic separation (repeated, preparative chromatography was sometimes necessary).



	n	R	R'	Series
22	0	Ac	Bzl	D
23	1	Ac	Bzl	D
24	2	Ac	Bzl	D
25	3	Ac	Bzl	D
26	4	Ac	Bzl	D
27	0	Ac	H	E
28	1	Ac	H	E
29	2	Ac	H	E
30	3	Ac	H	E
31	4	Ac	H	E
32	0	Ac	Ac	F
33	1	Ac	Ac	F
34	2	Ac	Ac	F
35	3	Ac	Ac	F
36	4	Ac	Ac	F

	n	R	R'	Series
37	0	H	H	G
38	1	H	H	G
39	2	H	H	G
40	3	H	H	G
41	4	H	H	G
42	0	Me	Me	H
43	1	Me	Me	H
44	2	Me	Me	H
45	3	Me	Me	H
46	4	Me	Me	H
47	2	H	Bzl	

Catalytic hydrogenolysis of the benzyl groups from the condensation products **7–11** and **22–26** followed by acetylation gave the peracetates **17–21** and **32–36**. To obtain the title methyl β-glycosides of xylodextrins, compounds **32–36** or their precursors **27–31** were deacetylated.

TABLE I

^{13}C-N.M.R. SPECTRAL DATA FOR **4**, **7–41**, AND **47**

Compound	*Ring*	*Chemical shifts (p.p.m.)*					
		C-1	*C-2*	*C-3*	*C-4*	*C-5*	*Me*
4	C-α[a]	90.1	71.2	71.6	75.4	59.4	
	C-β	95.5	73.2	73.7	75.1	63.8	
7	C	101.7	71.1	72.8	74.3	63.9	56.7
	C′	96.2	70.8	71.7	75.4	60.0	
8	C	101.9	70.1	72.6	75.9	63.8	56.8
	C′	100.6	70.8	72.4	73.6	63.0	
	C″	96.5	70.1	71.5	75.4	60.0	
9	C	101.9	71.1	72.6	75.5	63.7	56.7
	C′	100.4	70.9	72.0	74.9	62.5	
	C″	100.4	70.8	72.5	73.5	63.0	
	C‴	96.4	71.1	71.4	75.3	60.0	
10	C	101.8	71.2	72.6	75.6	63.7	56.8
	C′	100.3	71.0	72.0	74.9	62.5	
	C″	100.3	70.9	72.0	74.9	62.5	
	C‴	100.3	70.7	72.5	73.5	63.0	
	C⁗	96.4	71.2	71.4	75.2	60.0	
11	C	101.9	71.2	72.6	75.6	63.7	56.8
	C′	100.3	70.8	72.0	74.9	62.5	
	C″	100.3	70.8	72.0	74.9	62.5	
	C‴	100.3	70.8	72.0	74.9	62.5	
	C⁗	100.3	70.8	72.4	73.5	62.9	
	C⁗′	96.4	71.2	71.4	75.3	60.0	
12	C	101.7	71.7	72.9	74.3	64.0	56.7
	C′	96.4	70.9	72.9	68.7	61.9	
13	C	101.9	71.1	72.6	75.7	63.9	56.9
	C′	100.5	70.8	72.6	73.8	63.0	
	C″	96.3	71.6	72.6	68.6	61.9	
14	C	101.9	71.2	72.7	75.7	63.9	56.9
	C′	100.4	70.9	72.1	75.1	62.7	
	C″	100.4	70.8	72.7	73.7	62.9	
	C‴	96.4	71.6	72.7	68.7	62.0	
15	C	101.8	71.1	72.5	75.5	63.8	56.8
	C′	100.3	70.8	71.9	74.9	62.5	
	C″	100.3	70.8	71.9	74.9	62.5	
	C‴	100.3	70.5	72.5	73.7	62.9	
	C⁗	96.4	71.4	72.9	68.9	61.9	
16	C	102.1	71.3	72.7	75.7	64.0	57.0
	C′	100.5[a]	71.0	72.0	75.1	62.6	
	C″	100.5[a]	71.0	72.0	75.1	62.6	
	C‴	100.5[a]	71.0	72.0	75.1	62.6	
	C⁗	100.5[a]	70.6	72.7	73.8	63.0	
	C⁗′	96.6	71.5	73.4	69.2	62.0	
17	C	101.7	71.5	73.1	73.9	63.8	56.9
	C′	96.2	70.8	69.1	69.1	58.7	
18	C	101.9	71.2	72.8[b]	75.6	63.4	56.8
	C′	100.3	70.8	72.6[b]	73.2	62.9	
	C″	96.3	71.2	69.0	69.0	58.8	

TABLE I *(continued)*

Compound	*Ring*	*Chemical shifts (p.p.m.)*					
		C-1	*C-2*	*C-3*	*C-4*	*C-5*	*Me*
19	C	101.9	71.1	72.7	75.6	63.4	56.9
	C′	100.4[b]	70.8	72.0	75.0	62.7	
	C″	100.3[b]	70.8	72.7	73.2	62.9	
	C‴	96.4	71.1	69.0	69.0	58.8	
20	C	101.9	71.2	72.6	75.6	63.5	56.8
	C′	100.3	70.8	71.9	74.9	62.5	
	C″	100.3	70.8	71.9	74.9	62.5	
	C‴	100.3	70.8	72.6	73.2	63.0	
	C⁗	96.3	71.2	69.0	69.0	58.8	
21	C	101.9	71.2	72.7	75.6	63.4	56.8
	C′	100.3	70.8	72.0	75.0	62.5	
	C″	100.3	70.8	72.0	75.0	62.5	
	C‴	100.3	70.8	72.0	75.0	62.5	
	C⁗	100.3	70.8	72.7	73.2	63.0	
	C⁗′	96.3	71.2	69.0	69.0	58.8	
22	C	101.9	71.2	72.8	75.7	63.2	56.8
	C′	100.6	71.2	72.8	74.3	63.0	
23	C	101.9	71.2	72.9	75.5	62.9	56.8
	C′	100.4	70.8	72.0	74.3	62.5	
	C″	100.4	71.2	72.9	75.0	63.3	
24	C	101.9	71.2	72.9	75.5	62.9	56.9
	C′	100.4	70.8	71.9	75.0	62.5	
	C″	100.4	70.8	71.9	74.3	62.5	
	C‴	100.4	71.2	72.9	75.0	63.3	
25	C	101.9	71.1	72.8	75.6	62.8	56.9
	C′	100.4	70.8	71.9	74.7	62.4	
	C″	100.4	70.8	71.9	74.7	62.4	
	C‴	100.4	70.8	71.9	74.3	62.4	
	C⁗	100.4	71.1	72.5	74.7	63.3	
26	C	101.9	71.1	72.8	75.5	62.8	56.8
	C′	100.2[a]	70.8	71.8	74.9	62.5	
	C″	100.2[a]	70.8	71.8	74.9	62.5	
	C‴	100.2[a]	70.8	71.8	74.9	62.5	
	C⁗	100.2[a]	70.8	71.8	74.3	62.5	
	C⁗′	100.2[a]	71.1	72.5	74.9	63.2	
27	C	102.0	71.2	72.6	75.2	62.9	56.9
	C′	99.9	70.3	74.2	67.8	64.5	
28	C	102.1	71.4	72.8	75.8	63.1	57.0
	C′	100.7	71.2	72.3	74.5	62.8	
	C″	100.3	70.7	74.7	67.9	64.8	
29	C	101.9	71.1	72.5	75.5	62.9	56.8
	C′	100.3	70.9	72.0	74.9	62.6	
	C″	100.3	70.9	72.0	74.4	62.6	
	C‴	100.0	70.5	74.9	67.7	64.6	
30	C	102.1	71.2	72.7	75.8	62.9	57.0
	C′	100.5	71.0	72.1	74.9	62.6	
	C″	100.5	71.0	72.1	74.9	62.6	
	C‴	100.5	71.0	72.1	74.4	62.6	
	C⁗	100.1	70.5	74.9	68.0	64.7	

TABLE I *(continued)*

Compound	*Ring*	*Chemical shifts (p.p.m.)*					
		C-1	*C-2*	*C-3*	*C-4*	*C-5*	*Me*
31	C	101.9	71.2	72.6	75.7	62.9	56.8
	C′	100.3	71.0	72.0	74.9	62.6	
	C″	100.3	71.0	72.0	74.9	62.6	
	C‴	100.3	71.0	72.0	74.9	62.6	
	C⁗	100.3	71.0	72.0	74.4	62.6	
	C⁗′	99.7	70.5	74.9	67.9	64.7	
32	C	102.0	71.3	72.6	75.1	62.9	56.8
	C′	99.7	70.4	70.4	68.4	61.6	
33	C	101.9	71.1	72.5	75.6	62.9	56.9
	C′	100.5	71.1	71.9	74.2	62.5	
	C″	99.5	70.2	70.2	68.2	61.6	
34	C	102.1	71.3	72.7	75.7	63.0	57.0
	C′	100.6	71.0	72.0	74.9	62.6	
	C″	100.6	71.0	72.0	74.3	62.6	
	C‴	99.7	70.4	70.4	68.4	61.6	
35	C	102.1	71.3	72.7	75.7	62.9	57.0
	C′	100.6	71.0	72.1	74.9	62.6	
	C″	100.6	71.0	72.1	74.9	62.6	
	C‴	100.6	71.0	72.1	74.3	62.6	
	C⁗	99.7	70.4	70.4	68.4	61.7	
36	C	102.1	71.3	72.7	75.7	63.1	57.0
	C′	100.4[a]	71.0	71.9	75.0	62.6	
	C″	100.4[a]	71.0	71.9	75.0	62.6	
	C‴	100.4[a]	71.0	71.9	75.0	62.6	
	C⁗	100.4[a]	71.0	71.9	74.3	62.6	
	C⁗′	99.5	70.5	70.5	68.4	61.7	
37	C	105.1	74.0	75.0	77.7	64.1	58.4
	C′	103.1	74.0	76.9	70.4	66.5	
38	C	105.1	74.1	75.0	77.7	64.1	58.3
	C′	103.0	74.1	75.0	77.7	64.3	
	C″	103.1	74.0	76.9	70.4	66.5	
39	C	105.1	74.1	75.0	77.6	64.2	58.5
	C′	103.0	74.1	75.0	77.6	64.2	
	C″	103.0	74.1	75.0	77.6	64.2	
	C‴	103.1	74.1	76.9	70.4	66.5	
40	C	105.0	74.0	74.9	77.6	64.2	58.4
	C′	102.9	74.0	74.9	77.6	64.2	
	C″	102.9	74.0	74.9	77.6	64.2	
	C‴	102.9	74.0	74.9	77.6	64.2	
	C⁗	102.9	74.0	76.8	70.4	66.5	
41	C	105.3	74.0	75.0	77.7	64.2	58.5
	C′	103.1	74.0	75.0	77.7	64.2	
	C″	103.1	74.0	75.0	77.7	64.2	
	C‴	103.1	74.0	75.0	77.7	64.2	
	C⁗	103.1	74.0	75.0	77.7	64.2	
	C⁗′	103.1	74.0	76.9	70.5	66.5	
47	C	105.1	74.1	75.0	77.6	64.2	58.5
	C′	103.0	74.1	75.0	77.6	64.2	
	C″	103.0	74.1	75.0	77.6	64.2	
	C‴	103.0	74.1	76.1	78.4	64.2	

[a]These resonances are slightly resolved. [b]These resonances may be reversed.

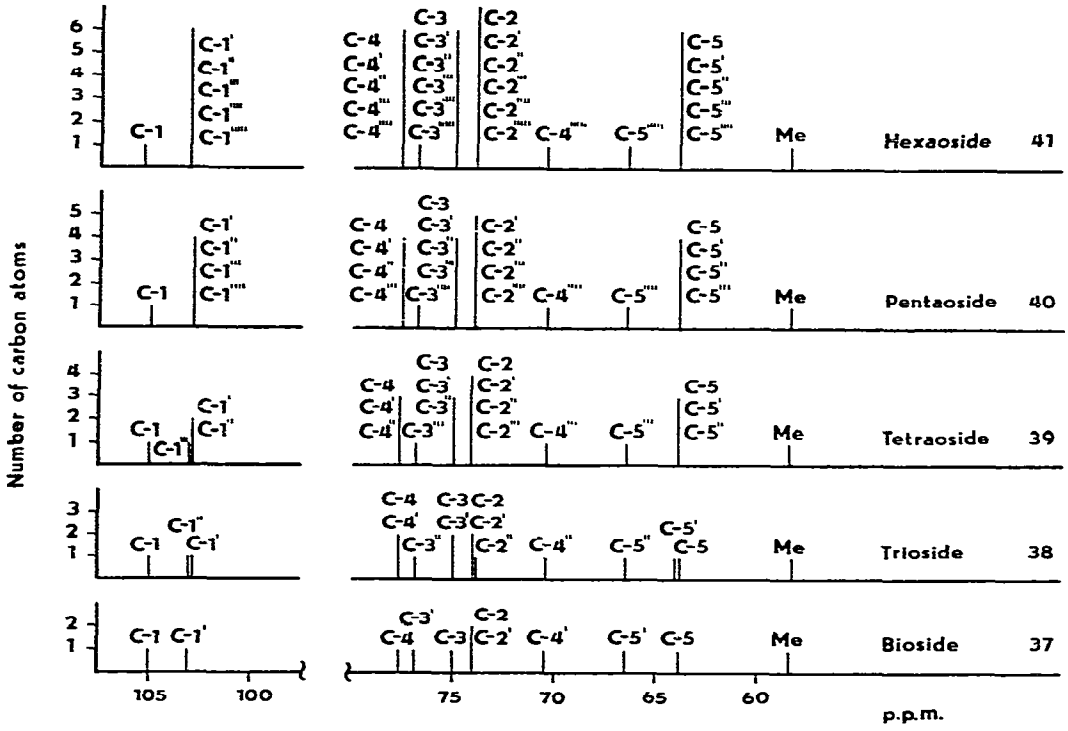


Fig. 1. Comparison of ^{13}C-n.m.r. spectra of methyl β-glycosides of (1→4)-β-D-xylo-oligosaccharides

Compounds **7**–**46** form eight homologous series of variously substituted methyl β-glycosides of (1→4)-D-xylo-oligosaccharides (Series A–H, see accompanying formulae) differing in the configuration of the interglycosidic linkage at the non-reducing D-xylosyl end-group. Disaccharides of Series C and F–H (**17**, **32**, **37**, and **42**) and trisaccharides of Series F–H (**33**, **38**, and **43**) have been previously described in this Series. The known compounds independently synthesised during this work were identical with previously described substances. Compounds that were hitherto unknown were characterised by physical constants, and their structures confirmed from analysis of ^{13}C-n.m.r. spectra. The number of sugar units in their molecules was further confirmed by the presence of ion-peaks of Series A in the mass spectra of the fully methylated substances **42**–**44**, from which their molecular mass could be calculated[12,13].

^{13}C-N.m.r. spectroscopy. — Chemical shifts for the first two members of the homologous series of β-glycosides of (1→4)-β-D-xylo-oligosaccharides have been reported[14]. The spectral characteristics observed for substances of Series G (Table I) are in full agreement with the variations of line intensity expected for oligosaccharides belonging to the same homologous series[15]. The line spectra of the title glycosides **37**–**41** (Fig. 1) clearly show identity, or close similarity, of chemical shifts for equivalent

carbon atoms of the internal residues, and an increase in the relative intensity of these signals with the increasing number of D-xylosyl residues in the molecule.

The analysis of spectra of oligosaccharides of the other homologous series is based on comparisons of diagnostically important regions in the spectra of substances belonging to individual series. Signal assignments for peracetates of the title oligosaccharides, based on the similarity of chemical shifts for equivalent carbon atoms of internal residues, according to which the lines associated with them can be distinguished from those due to carbons of the terminal groups, are exemplified in Fig. 2. The line spectra of methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-β-D-xylopyranoside and methyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (Fig. 3) were used as an additional aid in the assignments. The assignment of lines at δ 102.0 and 99.7 in the spectrum of the disaccharide, and those at δ 75.6 and 74.2 in the spectrum of the trisaccharide, to C-1 and C-1′, and to C-4 and C-4′, respectively, is based on comparisons of chemical shifts of lines appearing in these diagnostically significant regions in the spectra of substances of all Series (Table I). The spectra of monosaccharide model-compounds

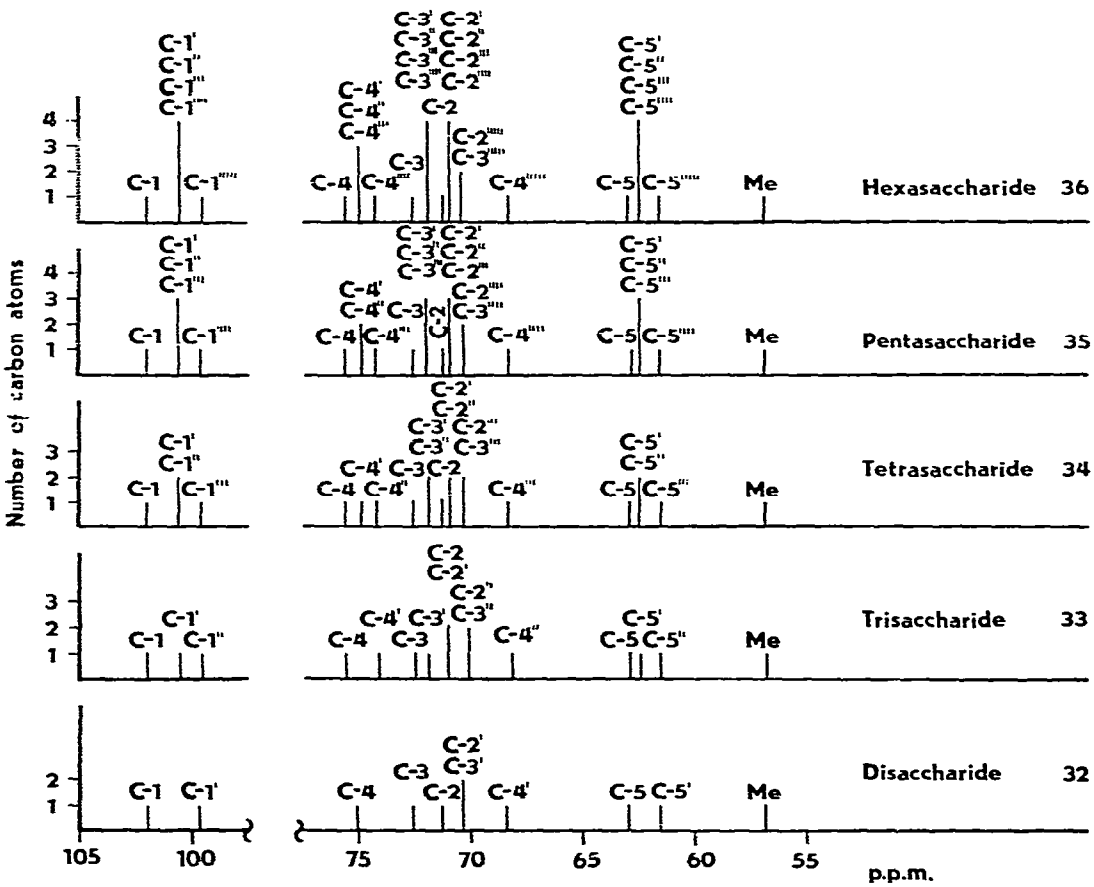


Fig. 2. Comparison of line spectra of peracetates of methyl β-glycosides of β-xylodextrins.

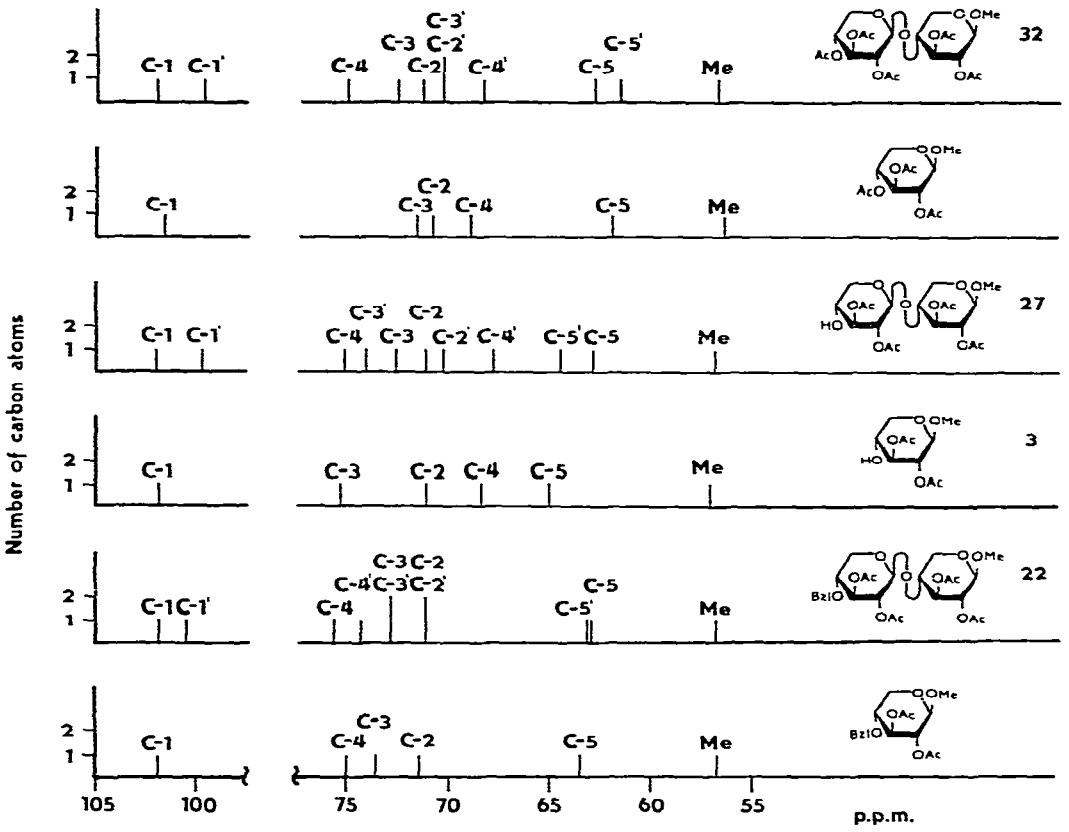


Fig. 3. Comparison of diagnostically significant shifts of lines in the ^{13}C-n.m.r. spectra of disaccharides of Series D–F with similar shifts in the spectra of model monosaccharide derivatives.

did not help in the assignment of lines at δ 71.3–70.4 in the spectra of oligosaccharides. These were identified in a reciprocal manner, using spectra of higher oligosaccharides to confirm assignments in the spectra of lower members in the same Series, in a manner similar to that used for cellobiose with the aid of spectra of cello-oligosaccharides[15]. For example, considering only spectra of monosaccharides (Fig. 3), it was difficult to decide whether the signal at δ 71.3 in the spectrum of methyl penta-*O*-acetyl-β-xylobioside is due to C-2 or C-3′ or, in other words, whether the two-carbon signal at δ 70.4 is a coincidence of signals for either C-2 and C-2′ or C-2′ and C-3′. Without the aid of the spectra of higher oligosaccharides, the assignment of lines to C-2 and C-3′ would probably be the reverse of that shown in Fig. 2, since, because of their same position relative to the glycosidic linkage, C-2 and C-2′ might be expected[15] to resonate at a similar magnetic field and therefore it would not be surprising if signals for C-2 and C-2′ were unresolved. However, if the assignment of the line at δ 70.4 to C-2 and C-2′ is correct (*i.e.*, if the C-2 atoms of all D-xylose residues in compounds of Series F are magnetically equivalent), the intensity of the line at ~70

p.p.m. would have to increase with increasing chain-length of the oligosaccharide. The line spectra in Fig. 2 show that the intensity of this line remains constant throughout the spectra of oligosaccharides of Series F. Except for the signals of C-2 and C-2′ in the spectrum of the trisaccharide, which coincide at δ 71.1, signals for C-2 of the internal residues produce a separate, joint signal. Starting with the tetrasaccharide, the spectra of the higher oligosaccharides show signals at δ 71.3 and 71.0. While the intensity of the former remains constant throughout the series, that of the latter increases with increasing chain-length. Therefore, the signals at δ 71.3 and 71.0 can be confidently assigned to C-2 of the reducing end-unit and C-2 of the internal residues, respectively.

The correct assignment of signals to carbon atoms of the non-reducing end-groups of oligosaccharides was further confirmed by following, in the spectra of oligosaccharides of different Series, the shifts of lines as a result of chemical modification. In order to monitor changes resulting from hydrogenolysis of the benzyl group at the non-reducing end of an oligosaccharide and subsequent acetylation of the free hydroxyl groups (conversion of the respective oligosaccharides of Series D→E→F), the spectra of methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-β-D-xylopyranoside, methyl 2,3-di-*O*-acetyl-β-D-xylopyranoside, and methyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside were used as an aid. The monitoring of analogous changes of positions of lines in the spectra of oligosaccharides of Series A–C containing an α-linked, terminal D-xylosyl group was aided by spectra of the corresponding derivatives of methyl α-D-xylopyranoside[16]. These monosaccharide derivatives simulate the terminal, non-reducing end-group of the oligosaccharides. An example of this means of line-assignment in the spectra of disaccharides of Series D–F is depicted in Fig. 3. In the spectra of the model monosaccharides, loss of the benzyl group removes the strong, positive α- and medium, negative β-effects of alkylation[17]. As a result, compared with the spectrum of methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-β-D-xylopyranoside, the spectrum of methyl 2,3-di-*O*-acetyl-β-D-xylopyranoside shows shifts of signals corresponding to C-4 (δ 75.0→68.4), C-3 (73.6→75.4), and C-5 (63.5→65.1). On subsequent acetylation of HO-4, C-4, C-3, and C-5 are exposed to the effects of the acetoxyl group[16–18] at C-4 (a weak, positive α-effect and a somewhat stronger, negative β-effect). As a consequence, the spectrum of methyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside shows shifts of signals for C-4 (δ 68.4→69.0), C-3 (75.4→71.6), and C-5 (65.1→62.0). In the spectra of disaccharides **22**, **27**, and **32**, similar shifts are noticeable (Fig. 3). That the effect of the benzyl group is similar to that of 2,3-di-*O*-acetyl-4-*O*-benzyl-β-D-xylopyranosylation in **22** is shown by the identical or very close chemical shifts observed for C-2 and C-2′, C-3 and C-3′, and C-5 and C-5′ in the spectrum of **22**. On the other hand, the different shift-effects of α- and β-D-xylopyranosylation are shown by a comparison of the spectral data for **22** and **7** (Table I). In the spectrum of **7** (α-interglycosidic linkage), each carbon nucleus produces a separate signal, and the diagnostically significant difference between the magnitude of the negative β-effects at C-5 of α- and β-glycosylation is exceptionally easy to recognise (see below). As a result of effects discussed above, removal of the benzyl group from **22**, to give **27**,

causes a shift of signals for C-3′ (δ 72.8→74.2), C-4′ (74.3→67.8), C-5′ (63.2→64.5), and C-2′ (71.2→70.3). Acetylation of HO-4′ in **27**, to give **32**, shifts the line at δ 74.2, for C-3′, to higher field at δ 70.4. Thus, at this δ value, a two-carbon signal is observed. Similarly, on account of the negative β-effect of the acetyl group, the C-5′ signal at δ 64.5, for **27**, is shifted upfield to δ 61.6, for **32**.

The ^{13}C-n.m.r. spectra showed regularities which could be used to confirm the configuration at the newly formed, inter-sugar linkage, tentatively assigned on the basis of specific optical rotation. From this viewpoint, the diagnostically most significant signals were those for C-1 and C-5. Compounds containing only β linkages show (Table I) anomeric resonances at δ ~102.0 and 100.1–100.6. The high-field signal, whose intensity increases with increasing chain-length, is easily recognised to be that of C-1 of internal residues. The line at δ ~102.0, present in the spectra of all compounds of Series A–F as a one-carbon signal, is associated with C-1 of the reducing end-group. In the region of C-5 resonances, the spectra of compounds containing only β-interglycosidic linkages show, starting with the trisaccharide, three lines at δ 63.3, 62.9, and 62.5. The intensity of the two low-field signals, also present in the spectrum of the disaccharide, remains unchanged throughout Series D, and they were therefore assigned to the terminal D-xylose residues. As the number of β-D-xylopyranosyl residues increases, the intensity of the signal at δ 62.5, due to C-5 of internal residues, also increases. Condensation products which contain an α-linked, terminal, non-reducing D-xylosyl group (A Series) produce, starting with the trisaccharide, three anomeric carbon signals, of which two (δ 101.7–101.9 and 100.3–100.6) show virtually the same chemical shifts as those of oligosaccharides of Series D. As in the spectra of Series D compounds, the intensity of the resonance at δ 100.3–100.6 increases with an increase in the number of β-linked D-xylosyl residues in the oligomer, and it can therefore be assigned to the internal residues. The diagnostically important C-1 signal of the terminal, non-reducing α-D-xylosyl group in oligosaccharides of Series A–C appears at δ 96.2–96.5. The presence of the terminal, non-reducing 2,3-di-*O*-acetyl-4-*O*-benzyl-α-D-xylopyranosyl group in oligosaccharides of Series A was also evident from the chemical shifts of the C-5 nuclei. Signals for C-5 of the reducing and non-reducing, terminal D-xylose residues appear in the spectra of compounds of this Series at ~63.7 and 60.0 p.p.m., respectively. The difference between the shift effect of 2,3-di-*O*-acetyl-4-*O*-benzyl-β-D-xylopyranosidation and similar α-glycosidation is reflected by the appearance in the spectrum of the trisaccharide **8** of a new line at δ 63.0, assigned to C-5 of the internal unit. In the spectra of higher oligosaccharides of Series A, another new line appears between the resonances for C-5 of the terminal and the penultimate units of the oligomer (numbering from the reducing end-unit). The intensity of this resonance increases with increasing chain-length and it was therefore assigned to those β-linked D-xylosyl residues that carry a β-linked D-xylose residue at O-4.

Of the other features shown by the spectra of the homologous Series A–F of oligosaccharides, the following regularities found for C-4 and C-3 resonances are noteworthy. The C-4 nuclei of the reducing end-unit of higher oligosaccharides of all

Series produce a separate signal within the range δ 75.1–75.9. A separate signal at δ 73.2–74.4 is also produced by C-4 of the penultimate D-xylosyl residue of substituted methyl β-glycosides of oligosaccharides. It diagnostically significant chemical-shift reflects the difference between the α-effects of α- and β-D-xylosidation: whereas compounds containing an α-D-xylopyranosyl group attached to O-4 of the penultimate β-D-xylosyl residue (those of Series A–C) show the C-4 line of this residue at δ 73.2–73.9, C-4 of the penultimate β-D-xylosyl residue of compounds having a β-D-xylosyl group linked at this position resonates at δ 74.2–74.4 (Table I). The C-4 resonances of all other internal β-linked units of oligosaccharides are coincident. The chemical shift for C-4 of the non-reducing D-xylosyl group depends, of course, upon the effect of the substituent at this position (*cf.* Fig. 3 and Table I). For compounds in Series D, the C-4 signal of the terminal, non-reducing β-D-xylosyl residue benzylated at this position coincides with that of C-4 of the internal residues (at ~75.0 p.p.m.), and the corresponding resonance of their α-linked counterparts appears slightly downfield, in a very narrow range, at δ 75.2–75.4. Thus, the spectra of substances of series A show two lines in the range δ 75.0–76.0, corresponding to C-4 of the two terminal D-xylosyl groups. Compounds of Series B, C, E, and F show the C-4 signal of the non-reducing, terminal D-xylosyl group at δ <69.2. Characteristic of compounds of Series C is a two-carbon signal at δ 69.0, due to the coincidence of the C-3 and C-4 signals of the fully acetylated, non-reducing, terminal α-D-xylosyl group.

Throughout the Series of oligosaccharides studied, the chemical shifts of the C-3 nuclei depend markedly on the type of substituent at the neighbouring position 4, and also on the stereochemistry of the interglycosidic linkage at that site, when the substituent is a glycosyloxy group. Signals for C-3 of the reducing end-group appear at δ 72.4–72.9, and those of all internal residues appear at ~72.0 p.p.m. Resonances of the penultimate pyranosyl residues that bear an α-D-xylosyloxy group at C-4 are shifted slightly downfield (by ~0.5 p.p.m.).

Depending upon the substitution at HO-4, the C-3 signal of the terminal, reducing end-group appears (Table I) at a relatively wide range of δ values; for compounds of Series F, having the neighbouring HO-4 free, this C-3 signal is shifted downfield, and coincides with the C-4 signal of the internal residues.

In contrast to the title oligosaccharides, which produce virtually one joint line for C-2 of all β-D-xylosyl groups (*cf.* Fig. 1), the C-2 resonances of the substituted oligosaccharides form a more complicated pattern. The differences among the chemical shifts for C-2 of the individual D-xylopyranosyl residues may be a result of long-range effects or may result from differences in linkage conformation or solvation at the individual interglycosidic linkages.

EXPERIMENTAL

General methods. — Melting points were determined on a Kofler hot-stage. Optical rotations (22°, *c* 1; for solutions of **4**, **5**, and compounds of Series A–F and H in chloroform, and for **47** and compounds of Series G in water) were measured with

a Perkin–Elmer Model 141 automatic polarimeter. Preparative chromatography was performed by gradient elution from columns of dry-packed Silica Gel 60 which, prior to packing, had been equilibrated with 40% of the mobile phase. All reactions were monitored by t.l.c. on Silica Gel G. Detection was made possible by charring with 5% sulfuric acid in ethanol.

Mass spectra (12 eV) were obtained as previously described[12]. The ^{13}C-n.m.r. spectra were recorded at room temperature with Jeol JNM FX-60 and FX-100 spectrometers, in the deuterium-lock mode. Spectra for compounds in Series A–F were recorded for solutions in $CDCl_3$ (internal Me_4Si), and for **47** and compounds in Series G for solutions in D_2O (internal MeOH, δ(MeOH) *vs.* Me_4Si, 50.15). The solution of hydrogen bromide used contained 0.1 g of HBr/mL. Microanalyses were performed with a Perkin–Elmer Model 240 automatic analyser. Toluene and acetonitrile were dried with sodium hydride and calcium hydride, respectively, and freshly distilled. Dichloromethane was dried with phosphorus pentaoxide, and freshly distilled. Solutions were dried with anhydrous sodium sulfate and concentrated at 40°/2kPa. The given melting-points are values that did not change on further recrystallisation.

Oligosaccharides of Series A and D. — A solution of hydrogen bromide in dichloromethane (90 mL) was added to a solution of **1** (14.65 g, 40 mmol) in toluene (100 mL), and the mixture was left at room temperature for 15 min. After concentration and co-evaporation with toluene, a solution of the crude bromide **2** in the minimum amount of acetonitrile was added to a stirred mixture of **3** (5 g, 20 mmol) and mercuric cyanide (5.1 g, 20 mmol) in acetonitrile (85 mL), and stirring was continued for 1 h. T.l.c. (carbon tetrachloride–ethyl acetate, 4:1) then showed the absence of **2** (R_F 0.9) and the presence of only a trace of **3** (R_F 0.1). The main products had R_F 0.45–0.4 and 0.15. The mixture was processed conventionally and the crude product was chromatographed; eluted first from the zone of R_F 0.45–0.4 was **5**. Hydrogenolysis of **5** and acetylation of the product gave 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (**6**), m.p. 175–177°, $[\alpha]_D$ +38°; lit.[11] m.p. 175–176.5°, $[\alpha]_D$ +39.7°. Later fractions from the same zone contained a mixture of **5** and **7**, and crystallisation from ethanol gave methyl *O*-(2,3-di-*O*-acetyl-4-*O*-benzyl-α-D-xylopyranosyl)-(1→4)-2,3-di-*O*-acetyl-β-D-xylopyranoside (**7**; 2.4 g, 4.32 mmol), m.p. 149–161° (dimorphous substance; the large needles recrystallise at 155° to form silky crystals), $[\alpha]_D$ +140° (Found: C, 56.52; H, 6.21; OCH_3, 5.60. $C_{26}H_{34}O_{13}$ calc.: C, 56.30; H, 6.18; OCH_3 5.59%).

Eluted next was methyl *O*-(2,3-di-*O*-acetyl-4-*O*-benzyl-β-D-xylopyranosyl)-(1→4)-2,3-di-*O*-acetyl-β-D-xylopyranoside (**22**; 6.05 g, 10.9 mmol, 54.5%), m.p. 137–138° (from ethanol), $[\alpha]_D$ −85° (Found: C, 56.42; H, 6.26. $C_{26}H_{34}O_{13}$ calc.: C, 56.30; H, 6.18%).

The mother liquor remaining after crystallisation of **7** was hydrogenated as described in the preparation of compounds of Series B and E. The two products (R_F 0.5 and 0.2; chloroform–acetone, 8:1) were isolated by chromatography, to give 0.97 g (2.08 mmol; total yield of the α-linked disaccharide, 32%) of the faster-moving

12, which was identical with the substance obtained by hydrogenolysis of **7** (see below), and **5** which, when acetylated, afforded **6**, identical with the product described above.

Hydrolysis of **2** gave the hydroxy derivative **4**, which was obtained from the zone of R_F 0.15. It had m.p. 110–114° (from isopropyl ether), $[\alpha]_D$ +26° (Found: C, 59.23; H, 6.26. $C_{16}H_{20}O_7$ calc.: C, 59.25; H, 6.21%).

Similar condensations of **2** with nucleophiles **27–30** yielded the following products.

Compound **8** (27%), amorphous solid, $[\alpha]_D$ −18° (Found: C, 54.52; H, 6.04. $C_{35}H_{46}O_{19}$ calc.: C, 54.54; H, 6.01%).

Compound **23** (52.4%), m.p. 155–157° (from methanol), $[\alpha]_D$ −98° (Found: C, 54.72; H, 6.26. $C_{35}H_{46}O_{19}$ calc.: C, 54.54; H, 6.01%).

Compound **9** (30.2%), amorphous solid, $[\alpha]_D$ −37° (Found: C, 53.27; H, 5.84. $C_{44}H_{58}O_{25}$ calc.: C, 53.55; H, 5.92%).

Compound **24** (47.8%), m.p. 198–199° (from chloroform–methanol), $[\alpha]_D$ −106° (Found: C, 53.53; H, 6.07. $C_{44}H_{58}O_{25}$ calc.: C, 53.55; H, 5.92%). Deacetylation of **24**, as described for the preparation of compounds of Series G, yielded **47**, m.p. 236–237° (from methanol), $[\alpha]_D$ −84° (Found: C, 51.77; H, 6.42. $C_{28}H_{42}O_{17}$ calc.: C, 51.68; H, 6.50%).

Compound **10** (27.5%), amorphous solid, $[\alpha]_D$ −84.5° (Found: C, 52.72; H, 6.07. $C_{53}H_{70}O_{31}$ calc.: C, 52.90; H, 5.86%).

Compound **25** (42%), m.p. 236–239° (from acetonitrile–ethanol, or chloroform–methanol), $[\alpha]_D$ −110° (Found: C, 52.88; H, 5.94. $C_{53}H_{70}O_{31}$ calc.: C, 52.90; H, 5.86%).

Compound **11** (21%), amorphous solid, $[\alpha]_D$ −99° (Found: C, 52.71; H, 6.00. $C_{62}H_{82}O_{37}$ calc.: C, 52.46; H, 5.82%).

Compound **26** (39.5%), m.p. 247–250° (from chloroform–methanol), $[\alpha]_D$ −114° (Found: C, 52.22; H, 5.63. $C_{62}H_{82}O_{37}$ calc.: C, 52.46; H, 5.82%).

Oligosaccharides of Series B and F. — A mixture of **7** (1 g) and 5% palladium-on-charcoal (0.2 g) in acetone–methanol (1 : 1, 50 mL) was stirred in an atmosphere of hydrogen until t.l.c. showed that the reaction was complete (1–3 h). The mixture was processed conventionally, to give methyl *O*-(2,3-di-*O*-acetyl-α-D-xylopyranosyl)-(1→4)-2,3-di-*O*-acetyl-β-D-xylopyranoside (**12**; 0.8 g, 96%), m.p. 151–152° (from ethanol), $[\alpha]_D$ +21° (Found: C, 48.94; H, 6.18. $C_{19}H_{28}O_{13}$ calc.: C, 49.13; H, 6.08%).

Likewise, hydrogenolysis of **8–11** and **22–26** was carried out using, as solvent (according to the solubility of the substrate), the mixture as above, acetone, or *N*,*N*-dimethylformamide. The following products were obtained in virtually theoretical yields.

Compound **13**, amorphous solid, $[\alpha]_D$ −17° (Found: C, 49.19; H, 6.14. $C_{28}H_{40}O_{19}$ calc.: C, 49.41; H, 5.88%).

Compound **14**, amorphous solid, $[\alpha]_D$ −43° (Found: C, 49.29; H, 6.14. $C_{37}H_{52}O_{25}$ calc.: C, 49.55; H, 5.84%).

Compound **15**, amorphous solid, $[\alpha]_D$ −56° (Found: C, 49.92; H, 6.09. $C_{46}H_{64}O_{31}$ calc.: C, 49.63; H, 5.79%).

Compound **16**, amorphous solid, $[\alpha]_D$ −71° (Found: C, 49.78; H, 5.64. $C_{55}H_{76}O_{37}$ calc.: C, 49.69; H, 5.64%).

Compound **27**, m.p. 121–123° (from ethanol–ether), $[\alpha]_D$ −104° (Found: C, 49.43; H, 6.26. $C_{19}H_{28}O_{13}$ calc.: C, 49.13; H, 6.08%).

Compound **28**, m.p. 144–148° (from methanol containing a drop of chloroform), $[\alpha]_D$ −109° (Found: C, 49.35; H, 6.09. $C_{28}H_{40}O_{19}$ calc.: C, 49.41; H, 5.88%).

Compound **29**, m.p. 200.5–201.5° (from ethanol), $[\alpha]_D$ −113° (Found: C, 49.75; H, 6.28. $C_{37}H_{52}O_{25}$ calc.: C, 49.55; H, 5.84%).

Compound **30**, m.p. 236–238° (from chloroform–methanol), $[\alpha]_D$ −115° (Found: C, 49.27; H, 5.81. $C_{46}H_{64}O_{31}$ calc.: C, 49.63; H, 5.79%).

Compound **31**, m.p. 260–261° (from chloroform–methanol), $[\alpha]_D$ −115° (Found: C, 50.01; H, 5.84. $C_{55}H_{76}O_{37}$ calc.: C, 49.69; H, 5.76%).

Oligosaccharides of Series C and F. — Acetic anhydride (0.5 mL) was added to a solution of **12** (0.25 g) in pyridine (1.5 mL), and the mixture was left at room temperature for 18 h. Methanol was added (to decompose the excess of acetic anhydride) and, after conventional processing, chromatographically pure methyl *O*-(2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl)-(1→4)-2,3-di-*O*-acetyl-β-D-xylopyranoside (**17**: 0.25 g, 92%) was crystallised from methanol, and had m.p. 167–168°, $[\alpha]_D$ +27°, lit.[5] m.p. 168–169°, $[\alpha]_D$ +29.6°.

Similar acetylation of **13–16** and **27–31** afforded the following products in virtually theoretical yields.

Compound **18**, amorphous solid, $[\alpha]_D$ −16° (Found: C, 50.06; H, 6.12. $C_{30}H_{42}O_{20}$ calc.: C, 49.85; H, 5.85%).

Compound **19**, amorphous solid, $[\alpha]_D$ −38° (Found: C, 49.93; H, 6.07. $C_{39}H_{54}H_{26}$ calc.: C, 49.89; H, 5.79%).

Compound **20**, m.p. 240–241° (from chloroform–methanol), $[\alpha]_D$ −54.5° (Found: C, 50.20; H, 5.81. $C_{48}H_{66}O_{32}$ calc.: C, 49.91; H, 5.75%).

Compound **21**, amorphous solid, $[\alpha]_D$ −68° (Found: C, 50.12; H, 6.10. $C_{57}H_{78}O_{38}$ calc.: C, 49.92; H, 5.73%).

Compound **32**, m.p. 145–146° (from ethanol), $[\alpha]_D$ −94°, lit.[5] m.p. 145–146°, $[\alpha]_D$ −95°.

Compound **33**, m.p. 110–114° (from methanol), $[\alpha]_D$ −105°, lit.[8] m.p. 108–113°, $[\alpha]_D$ −105°.

Compound **34**, m.p. 245–246° (from chloroform–methanol), $[\alpha]_D$ −111° (Found: C, 50.12; H, 5.81. $C_{39}H_{54}O_{26}$ calc.: C, 49.89; H, 5.79%).

Compound **35**, m.p. 268–270° (from chloroform–methanol), $[\alpha]_D$ −115° (Found: C, 50.00; H, 6.99. $C_{48}H_{66}O_{32}$ calc.: C, 49.91; H, 5.75%).

Compound **36**, m.p. 278–280° (from chloroform–methanol), $[\alpha]_D$ −117° (Found: C, 49.87; H, 5.58. $C_{57}H_{78}O_{38}$ calc.: C, 49.92; H, 5.73%).

Oligosaccharides of Series G. — Methanolic M sodium methoxide was added to a solution of **32** (0.5 g) in methanol (50 mL) until the mixture was strongly alkaline,

and the mixture was kept at 40° for 2 h. After conventional processing, pure methyl 4-*O*-β-D-xylopyranosyl-β-D-xylopyranoside (methyl β-xylobioside, **37**) was obtained as a colourless foam (0.25 g, 86%), Crystallisation from ethanol yielded material having m.p. 148–149°; lit.[5] m.p. 103–104, 148.5–149, and 170–171°, for trimorphous **37**.

Deacetylation of **27** afforded **37** identical with the above-described substance, and similar treatment of **33–36** or **28–31** gave the following, title glycosides.

Methyl β-xylotrioside (**38**), m.p. 186–190° (from methanol); lit.[8] 190–191°.

Methyl β-xylotetraoside (**39**), m.p. 238–239° (from water–methanol), $[\alpha]_D$ −88° (Found: C, 45.12; H, 6.68. $C_{21}H_{36}O_{17}$ calc.: C, 49.99; H, 6.47%).

Methyl β-xylopentaoside (**40**), m.p. 234–236° (from water–methanol), $[\alpha]_D$ −90° (Found: C, 45.12; H, 6.51. $C_{26}H_{44}O_{21}$ calc.: C, 45.08; H, 6.40%).

Methyl β-xylohexaoside (**41**), m.p. 254–256° (from water–methanol), $[\alpha]_D$ −92° (Found: C, 44.97; H, 6.28. $C_{31}H_{52}O_{25}$ calc.: C, 45.14; H, 6.35%).

Oligosaccharides of Series H. — Sodium hydride (0.2 g) was added to a stirred solution of **39** (0.2 g) in *N*,*N*-dimethylformamide (2 mL) followed, after 15 min, by methyl iodide (0.5 mL), and the mixture was stirred, in the absence of atmospheric moisture and carbon dioxide, for 2 h. The mixture was diluted with water (5 mL), neutralised with 10% acetic acid, and partitioned between chloroform and water. The chloroform solution was concentrated with co-distillation of xylene, to remove *N*,*N*-dimethylformamide, and the crude product was eluted from a column of silica gel, to remove some undermethylated material. Methyl *O*-(2,3,4-tri-*O*-methyl-β-D-xylopyranosyl)-(1→4)-*O*-(2,3-di-*O*-methyl-β-D-xylopyranosyl-(1→4)-*O*-(2,3-di-*O*-methyl-β-D-xylopyranosyl)-(1→4)-2,3-di-*O*-methyl-β-D-xylopyranoside (**44**; 0.2 g, 81%), when crystallised from ether–hexane, had m.p. 122–124°, $[\alpha]_D$ −87° (Found: C, 52.28; H, 8.11. $C_{30}H_{54}O_{17}$ calc.: C, 52.46; H, 7.92%).

Similar methylation of **35** and **36** gave, in comparable yields: compound **45**, m.p. 122–124° (from chloroform–methanol), $[\alpha]_D$ −89° (Found: C, 52.23; H, 7.64. $C_{37}H_{66}O_{21}$ calc.: C, 52.47; H, 7.85%); and compound **46**, amorphous solid, $[\alpha]_D$ −91.5° (Found: C, 52.22; H, 7.57. $C_{44}H_{78}O_{25}$ calc.: C, 52.47; H, 7.81%).

ACKNOWLEDGMENTS

The authors thank M. Matulová for ^{13}C-n.m.r. measurements, K. Paule for microanalyses, and G. Košický for measurements of optical rotations.

REFERENCES

1 P. Kováč and J. Hirsch, *Carbohydr. Res.*, 79 (1980) 303–307.
2 P. Kováč and J. Hirsch, *Carbohydr. Res.*, 90 (1981) c5–c7.
3 T. E. Timell, *Wood Sci. Technol*, 1 (1967) 45–70.
4 P. Kováč, J. Hirsch, and V. Kováčik, *Chem. Zvesti*, 32 (1978) 514–518.
5 P. Kováč, *Collect. Czech. Chem. Commun.*, 45 (1980) 892–900.
6 P. Kováč, *Collect. Czech. Chem. Commun.*, 44 (1979) 928–932.
7 J. Hirsch and P. Kováč, *Carbohydr. Res.*, 77 (1979) 241–244.
8 P. Kováč, *Chem. Zvesti*, 34 (1980) 234–240.
9 P. Kováč and J. Alföldi, *Chem. Zvesti*, 32 (1978) 519–523.

10 P. KOVÁČ, A. ČULÁKOVÁ, E. PETRÁKOVÁ, AND J. HIRSCH, *Chem. Zvesti*, 35 (1981) 389–395.
11 B. HELFERICH AND W. OST, *Chem. Ber.*, 95 (1962) 2616–2622.
12 V. KOVÁČIK, V. MIHÁLOV, AND P. KOVÁČ, *Carbohydr. Res.*, 88 (1981) 189–201.
13 V. KOVÁČIK, V. MIHÁLOV, J. HIRSCH, AND P. KOVÁČ, *Biomed. Mass Spectrom.*, 5 (1978) 136–145.
14 P. KOVÁČ, J. HIRSCH, A. S. SHASHKOV, A. I. USOV, AND S. V. YAROTSKY, *Carbohydr. Res.*, 85 (1980) 177–185.
15 J. C. GAST, R. H. ATALLA, AND R. D. MCKELVEY, *Carbohydr. Res.*, 84 (1980) 137–146.
16 E. PETRÁKOVÁ AND P. KOVÁČ, *Carbohydr. Res.*, in press.
17 A. S. SHASHKOV AND O. S. CHIZHOV, *Bioorg. Khim.*, 2 (1976) 437–497.
18 J. P. UTILLE AND P. J. A. VOTTERO, *Carbohydr. Res.*, 85 (1980) 289–297.