^{13}C-NMR spectra of isomeric D-xylobioses

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^{13}C-N.m.r. spectra of a series of isomeric D-xylobioses were compared with those of mono-*O*-methyl- and mono-*O*-benzyl-D-xyloses. It has been found that, in terms of α effects, the benzyl group imitates β xylosylation better than does the methyl group; neither of these two substituents satisfactorily imitates α xylosylation. The α effect of D-xylosylation was found to be more positive in β-(1→2)- and β-(1→3)-linked D-xylobioses than in their α-linked counterparts; these relations were found to be reversed in (1→4)-linked substances. ^{13}C-N.m.r. spectra of mono-*O*-substituted derivatives of D-xylose (methyl, benzyl, and α- and β-D-xylopyranosyl) revealed regularities, depending upon the site of substitution, concerning the preponderating anomer present in an equilibrated aqueous solution. An alternative synthesis of 3-*O*-α- and 3-*O*-β-D-xylopyranosyl-D-xylose is also described. 4-*O*-Methyl-D-xylose was obtained for the first time in crystalline state.

Были сравнены ^{13}C-ЯМР спектры серии изомерных D-ксилобиоз с спектрами моно-*O*-метил и моно-*O*-бензил-D-ксилоз. Было обнаружено, что в смысле α-эффектов бензильная группа лучше имитирует β-ксилозилирование, чем метильная группа; ни который из этих заместителей не имитирует удовлетворительно α-ксилозилирование. В β-(1→2)- и β-(1→3)-вязанных дисахаридах α-эффект ксилозилирования является более положительным чем в соответствующих α-вязанных соединениях, причем в (1→4)-вязанных веществах эти отношения оборотные. В ^{13}C-ЯМР спектрах моно-*O*-замещенных производных D-ксилозы (метил-, бензил-и α- и β-D-ксилопиранозил) были обнаружены регулярности, касающиеся преимущества аномера, в зависимости от положения заместителей, в равновесном водном растворе. Описан тоже новый способ получения 3-*O*-α- и 3-*O*-β-D-ксилопиранозил-D-ксилоз. 4-*O*-Метил-D--ксилоза была в первый раз получена в кристаллическом состоянии.

Application of ^{13}C-n.m.r. spectroscopy facilitated the solution of such problems in carbohydrate chemistry as, for example, the determination of the site and the stereochemistry of intersugar linkages in oligo- and polysaccharides. Although the described empirical rules [1, 2] are useful for analyzing spectra of simple carbohy-

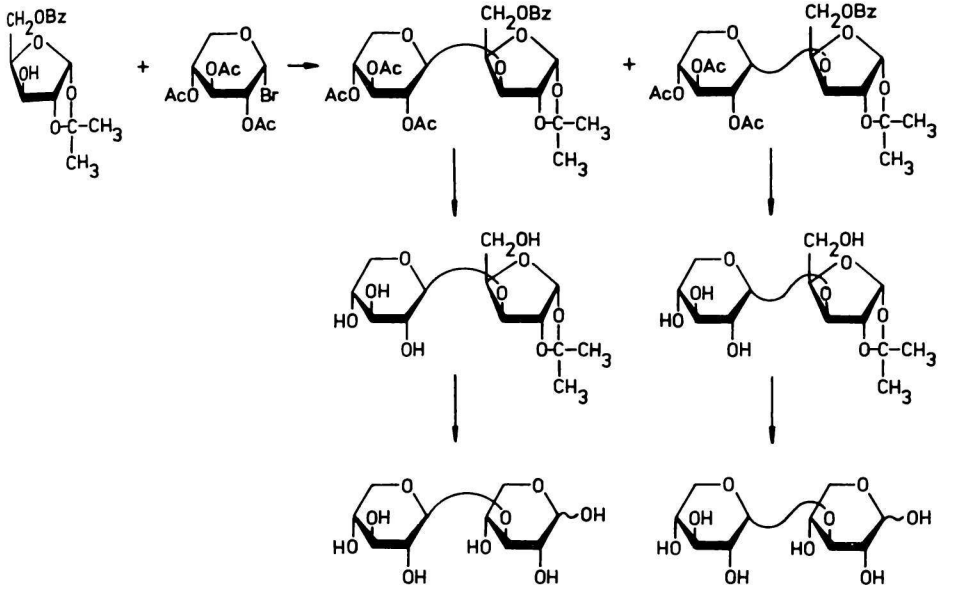
drate derivatives, lines in the spectra of complex oligosaccharides cannot be assigned reliably unless data from analyzed spectra of similar, less complex structures are available. Interpreted spectra of monosaccharide *O*-alkyl derivatives are of substantial help for the interpretation of spectra of disaccharides and, similarly, the assignment of lines in higher oligosaccharides can be accomplished with the aid of analyzed spectra of lower oligosaccharides.

We have previously published [3] spectra of methyl β-glycosides of isomeric D-xylooligosaccharides and have demonstrated their application to the structure elucidation of natural xylans. The conclusions arrived at on the basis of ^{13}C-n.m.r. data of xylans of known structures were in good agreement with those based on more tedious chemical analysis. We now present interpreted spectra of a complete series of isomeric *O*-α- and -β-D-xylopyranosyl-D-xyloses which are thought to be of importance for analyzing spectra of related free, higher or branched, D-xylooligosaccharides. Some of the data presented here assisted in the assignment of lines in the spectra of two branched D-xylotrioses, namely, 2-*O*-α- and -β-D-xylopyranosyl-4-*O*-β-D-xylopyranosyl-D-xylopyranoses [4].

Results and discussion

The studied (1→2)- and (1→4)-linked disaccharides were synthesized previously in our laboratory. The (1→3)-linked compounds were obtained *via* a new synthetic pathway (Scheme 1). Accordingly, 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide was condensed with 5-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-xylofuranose and the formed α- and β-linked disaccharide derivatives were isolated by chromatography. The crystalline substances (combined yield 75.6%, $\alpha : \beta = 1 : 2.3$) were debenzoylated and deisopropylidenated to give the desired, free disaccharides.

The ^{13}C-n.m.r. spectra of the series of D-xylobioses (Table 1) were interpreted using data obtained from the spectra of D-glucobioses [5, 6], methyl α- and β-D-xylopyranoside [1], a series of methyl β-glycosides of isomeric xylooligosaccharides [3] and mono-*O*-benzyl and mono-*O*-methyl derivatives of D-xylose (Table 1). *O*-Benzyl derivatives were only recently recommended, instead of more commonly used *O*-methyl derivatives, as more suitable for interpretation of spectra of some oligosaccharides composed of hexoses [7]. The studied mono-*O*-benzyl [8, 9] and mono-*O*-methyl [10] derivatives were prepared according to standard procedures. In the course of this work 4-*O*-methyl-D-xylose, the only compound of this series hitherto known only as a sirup, was for the first time obtained crystalline. The spectra of mono-*O*-alkyl derivatives were interpreted according to the common rules of ^{13}C-n.m.r. spectroscopy of carbohydrates, taking into account the α and β effects [1] of alkylation upon the chemical shift of signals



Scheme 1

of linkage carbon atoms, and carbon atoms at the neighbouring positions [1], respectively. Considered were also spectra of mono-*O*-methyl-D-glucoses [5] and the different line intensities corresponding to the carbon atoms of the individual anomeric forms of the substances. As far as the preponderating anomer in the equilibrated aqueous solution is concerned, a certain regularity was evident from the spectra which, within the series of substances under investigation, was observed for both monosaccharides and disaccharides. In the equilibrated aqueous solution of 3-*O*- and 4-*O*-substituted D-xylose derivatives (*O*-methyl-, *O*-benzyl-, and *O*-D-xylopyranosyl, regardless of the stereochemistry of the interglycosidic linkage) there is an appreciable preponderance of the β anomer. The difference in the amounts of the individual anomers present in equilibrated solutions of 2-*O*-methyl- and 2-*O*-benzyl-D-xyloses is almost nil, although the presence of a little more of the α anomer could be deduced from the spectra. In the case of the two (1→2)-linked disaccharides one anomer again clearly preponderates: in the equilibrated aqueous solution of the β-(1→2)-linked compound preponderates the α anomer, and the β anomer is the more abundant form in the solution of the α-(1→2)-linked substance. It is worth mentioning that the anomeric composition in equilibrated aqueous solutions of the pairs of anomers of the two substances [11, 4]:

Table 1

Chemical shifts (δ, p.p.m.) in the ^{13}C-n.m.r. spectra of mono-*O*-benzyl- and mono-*O*-methyl-D-xyloses, and isomeric D-xylobioses[a]

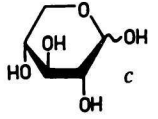
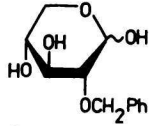
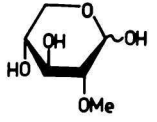
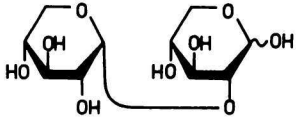
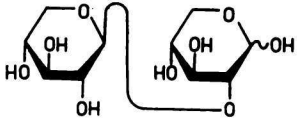
Compound	Ring[b] or anomer	Chemical shift					CH_2	Me
		C-1	C-2	C-3	C-4	C-5		
 *c*	α	93.3	72.5	73.9	70.4	62.1		
	β[d]	97.6	75.1	76.9	70.3	66.3		
	α[d]	91.4	80.0	73.3	70.5	61.8	73.3	
	β	98.0	83.2	76.6	70.6	66.2	75.7	
	α[d]	90.7	81.8	73.3	70.5	61.9		58.9
	β	97.7	84.9	76.5	70.7	66.3		61.4
	C-α	90.9	77.1	72.5	70.7	62.1		
	C-β[d]	98.2	79.4	75.6	70.7	66.2		
	C′-α	97.8	72.7	74.2	70.7	62.7		
	C′-β	99.0						
	C-α[d]	93.1	81.9	73.0	70.4	61.7		
	C-β	96.5	82.9	74.5	70.4	66.2		
	C′-α	105.9	74.3	76.7	70.4	66.2		
	C′-β	104.9						

Table 1 (Continued)

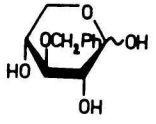
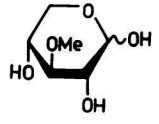
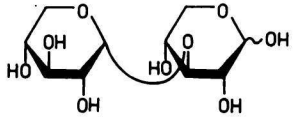
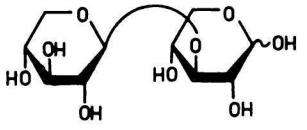
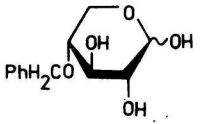
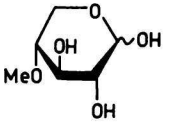
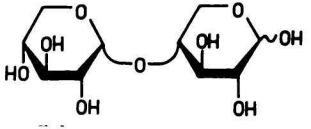
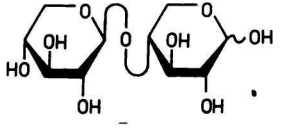
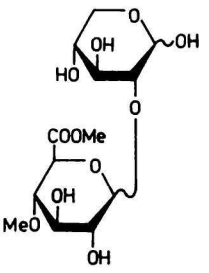
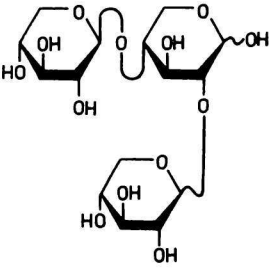
Compound	Ring[b] or anomer	Chemical shift					CH_2	Me
		C-1	C-2	C-3	C-4	C-5		
	α	93.7	72.4	82.3	70.4	62.5	76.0	
	β[d]	98.0	75.1	85.6	70.4	66.4	76.0	
	α	93.4	72.2	84.0	70.1	62.2		61.3
	β[d]	97.9	74.7	86.5	69.9	66.3		61.1
	C-α	93.6	70.8	80.1	70.6	62.4		
	C-β[d]	97.9	73.8	82.7	70.6	66.2		
	C′	100.0	72.8	74.3	71.1	62.7		
	C-α	93.3	72.1	82.9	68.9	62.1		
	C-β[d]	97.6	74.9	85.3	68.9	65.5		
	C′	104.7	74.6	76.8	70.4	66.3		
	α	96.4	72.8	73.3	78.4	60.4	74.3	
	β[d]	97.9	75.4	76.3	78.4	64.6	74.3	

Table 1 (Continued)

Compound	Ring[b] or anomer	Chemical shift					CH_2	Me
		C-1	C-2	C-3	C-4	C-5		
	α	93.4	72.8	73.0	80.0	59.8		59.5
	β[d]	97.9	75.4	76.1	80.0	64.1		59.5
	C-α	93.2	72.4[e]	72.9[e]	79.3	61.3		
	C-β[d]	97.7	75.1	76.1	79.3	65.5		
	C′	101.4	72.9	74.2	70.6	62.8		
	C-α	93.2	72.1[e]	72.6[e]	77.7	60.0		
	C-β[d]	97.7	75.1	75.1	77.6	64.1		
	C′	103.0	74.0	76.8	70.4	66.4		

a) Measured in D_2O; *b*) C — reducing unit, C′ — nonreducing unit; *c*) data taken from Ref. [1]; *d*) preponderating anomer in an equilibrated aqueous solution; *e*) the assignment may be reversed.





agrees with the above-mentioned observation, namely, in the solution of the α-(1→2)-linked aldobiouronic acid methyl ester preponderates the β anomer, and the α anomer is more abundant in the solution of the β-linked compound; similarly, in the case of the two branched D-xylotrioses (2-*O*-α- and -β-D-xylopyranosyl-4-*O*-β-D-xylopyranosyl-D-xylopyranoses) the preponderating species in the solution of β-(1→2)- and α-(1→2)-linked compounds is the α and β form, respectively. Thus, it appears that the 2-*O*-substitution is the dominating factor that decisively affects the establishment of the equilibrium between anomers in aqueous solution of free D-xylooligosaccharides.

The exceptional behaviour of 2-*O*-substituted D-xyloses originates from the proximity of the site of the substitution to the anomeric centre. It manifested itself in the ^{13}C-n.m.r. spectra also in another way, similar to the case of 2-*O*-methyl- and 2-*O*-D-glucopyranosyl-D-glucoses [5]. In the spectra of series of mono-*O*--methyl-D-glucoses and D-glucobioses the following anomalies have been recorded [5] with the 2-*O*-derivatives: of the series of monomethyl ethers only 2-*O*-methyl-D-glucose produced separate ^{13}C-n.m.r. signals for the carbon atom of the methyl group of the α and β form of the substances, and of the series of glucobioses only the spectra of kojibiose and sophorose (α-(1→2)- and β-(1→2)-linkage, respectively) showed separate signals for C-1$'_\alpha$ and C-1$'_\beta$ of the disaccharides. Similar characteristics were observed in the spectra of 2-*O*- and 3-*O*-methyl-D-xylose and in the spectra of (1→2)-linked xylobioses (Table 1). The assignments of signals at 61.4 and 58.9 p.p.m. to methoxyl carbon atoms of the β and α forms of 2-*O*-methyl-D-xylose were based on the line intensities. Similarly were assigned signals for methyl groups in the spectrum of 3-*O*-methyl-D-xylose, and also for the benzylic methylene groups of the α and β forms, in the spectrum of 3-*O*-benzyl-D-xylose, for which separate signals were observed at 73.3 and 75.7 p.p.m., respectively. The assignment of C-1′ signals in the spectra of (1→2)-xylobioses is discussed below.

An examination of the spectral data for model mono-*O*-methyl and mono-*O*-benzyl derivatives of D-xylose shows that the effects of methylation and benzylation upon the chemical shifts are not the same, they depend on both the site

of alkylation and the configuration at C-1, *i.e.* the alkylation affects chemical shifts of signals of carbon atoms of the individual anomeric forms in a different manner. The only regularity observed was that with the α effect (Table 2) which was consistently strongly more positive (a downfield shift of the signal of the linkage carbon atom) in the case of methylation than in the case of benzylation. A comparison of α effects of methylation, benzylation, and D-xylosylation (Table 2) reveals that, although not perfectly, the benzyl group imitates the β-interglycosidic linkage better than does the methyl group. For the studied α-linked disaccharides neither benzyl nor methyl group are satisfactory models.

A certain regularity was found between the magnitude of the α effect and the stereochemistry of the interglycosidic linkage: in (1→2)- and (1→3)-linked substances was the α effect of β-xylosylation more positive than that of α-xylosylation. The reverse was found to be true in the case of (1→4)-linked disaccharides. The same relations hold for (1→2)- and (1→3)-linked glucobioses [5]. The reversed dependence in the case of (1→4)-linked D-xylo- and D-glucobioses obviously results from the presence in the D-glucose molecule of a bulky substituent at C-5, a position adjacent to the site of linkage (C-5). The α effects of D-xylosylation in β-D-xylose and methyl β-D-xylopyranoside were found to be the same (since methyl α-glycosides of isomeric D-xylooligosaccharides were not available an analogous comparison of α effects in α-D-xylose and methyl α-D-xylopyranoside could not be made). Table 2 shows this comparison and also the fact that the shift effects of methylation and benzylation are far not as regular as those of D-xylosylation. The data from which the individual shift effects were calculated are in Table 3.

Of the spectra of the series of D-xylobioses only the ^{13}C-n.m.r. spectrum of β-(1→4) compound has been published and analyzed [6].* The spectrum recorded during this work was virtually identical with that of the previous authors. Small, insignificant differences between the recorded chemical shifts can be accounted for effects resulting from slightly different conditions of measurements. Similar to the case of β-(1→4)-D-xylobiose [6], spectra of the other D-xylobioses contain sets of signals of different intensity. Signals of carbon atoms of the nonreducing units were readily recognized according to their higher intensities, as compared with those associated with the reducing end-units which were weaker and reflected the anomeric composition in the equilibrated aqueous solutions. The line-assignments were facilitated by the known [3] ^{13}C-n.m.r. shifts found in the spectra of the corresponding methyl β-glycosides. The C-1′ signals of the (1→2)-linked disaccharides appeared as doublets, as did the C-1′ signals in the spectra of analogous

* The work appeared when the manuscript of this paper was in preparation.

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Table 2

Shift effects of benzylation, methylation, and D-xylosylation in α-D-xylose, β-D-xylose, and methyl β-D-xylopyranoside

Linkage carbon	$\Delta\delta$(OH—OCH_2Ph)	$\Delta\delta$(OH—OCH_3)	$\Delta\delta$(OH—O-α-D-xyl)	$\Delta\delta$(OH—O-β-D-xyl)
		α-D-Xylose		
C-2	7.5	9.3	4.6	9.4
C-3	8.4	10.1	6.2	9.0
C-4	8.0	9.6	8.9	7.3
		β-D-Xylose		
C-2	8.1	9.8	4.3	7.8
C-3	8.7	9.6	5.8	8.4
C-4	8.1	9.7	9.0	7.3
		Methyl β-D-xylopyranoside		
C-2	6.4	8.2	4.5	7.8
C-3	6.1	8.0	6.0	8.4
C-4	6.7	8.5	9.0	7.3

Table 3

Chemical shifts (δ, p.p.m.) in the ^{13}C-n.m.r. spectra of methyl mono-*O*-benzyl- and mono-*O*-methyl-β-D-xylopyranosides, and isomeric methyl β-D-xylobiosides[a]

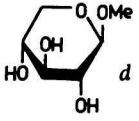
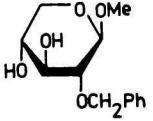
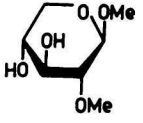
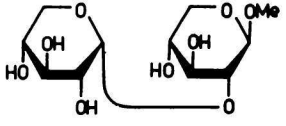
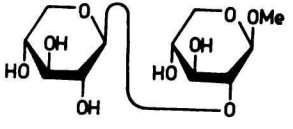
Compound	Ring[b]	Chemical shift[c]					CH_2	Methyl	
		C-1	C-2	C-3	C-4	C-5		acetal	ether
 *d*		105.1	74.0	76.9	70.4	66.3		58.3	
		104.3	80.4	74.9	69.5	64.8	74.2	56.7	
		104.1	82.2	74.9	69.6	64.8		56.7	60.3
	C C′	105.4 99.1	78.5 72.7	75.5 74.2	70.7 70.7	66.1 62.6		58.5	
	C C′	104.9 103.7	81.8 74.7	76.4 76.8	70.2 70.4	65.9 66.3		58.1	

Table 3 (Continued)

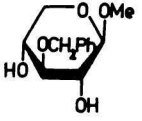
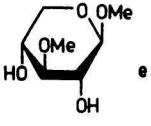
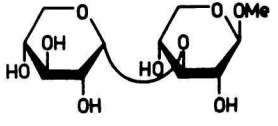
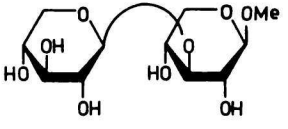
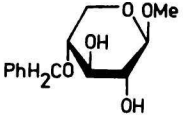
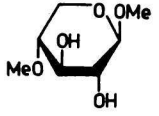
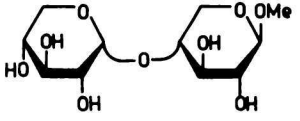
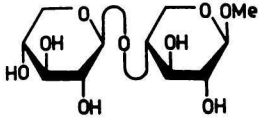
Compound	Ring[b]	Chemical shift[c]					CH_2	Methyl	
		C-1	C-2	C-3	C-4	C-5		acetal	ether
		104.2	73.0	83.0	69.1	65.0	74.3	56.9	
 e		104.3	73.1	84.9	69.0	65.0		57.1	60.5
	C C′	105.3 100.1	72.7 72.9	82.9 74.3	70.6 71.0	66.2 62.7		58.4	
	C C′	104.9 104.8	73.7 74.6	85.3 76.9	69.0 70.4	66.0 66.4		58.4	
		104.0	73.0	74.7	77.1	63.1	73.0	56.7	

Table 3 (Continued)

Compound	Ring[b]	Chemical shift[c]					CH_2	Methyl	
		C−1	C−2	C−3	C−4	C−5		acetal	ether
		103.9	72.6	73.9	78.9	62.1		56.7	58.5
	C C′	105.2 101.5	74.1 73.0	76.0 74.4	79.4 70.7	65.4 62.9		58.4	
	C C′	105.1 103.1	74.0 74.0	75.0 76.9	77.7 70.4	64.1 66.5		58.4	

a) Data for methyl glycosides of disaccharides taken from Ref. [3]; *b*) C — reducing unit, C′ — nonreducing unit; *c*) spectra of monosaccharide derivatives taken for solutions in $CDCl_3$, spectra of disaccharide derivatives taken in D_2O; *d*) data taken from Ref. [1]; *e*) data taken from Ref. [24].

D-glucobioses [5]. As a result, ^{13}C-n.m.r. spectra of these substances show four signals in the range of 90—106 p.p.m. Their assignment was developed as follows. The spectrum of 2-*O*-α-D-xylopyranosyl-D-xylose (Fig. 1) shows two signals of almost equal intensity at 99.0 and 98.2 p.p.m., and two weaker signals at 97.8 and 90.9 p.p.m. of which the former is more intense. The most intense signal of those at 62.1, 62.7, and 66.2 p.p.m. can be unequivocally assigned to C-5′, and it was obvious from the intensities of signals at 62.1 and 66.2 p.p.m. that β anomer is the preponderating anomer in the equilibrated solution. Since in the spectrum of methyl 2-*O*-α-D-xylopyranosyl-β-D-xylopyranoside (Table 3) the signal at

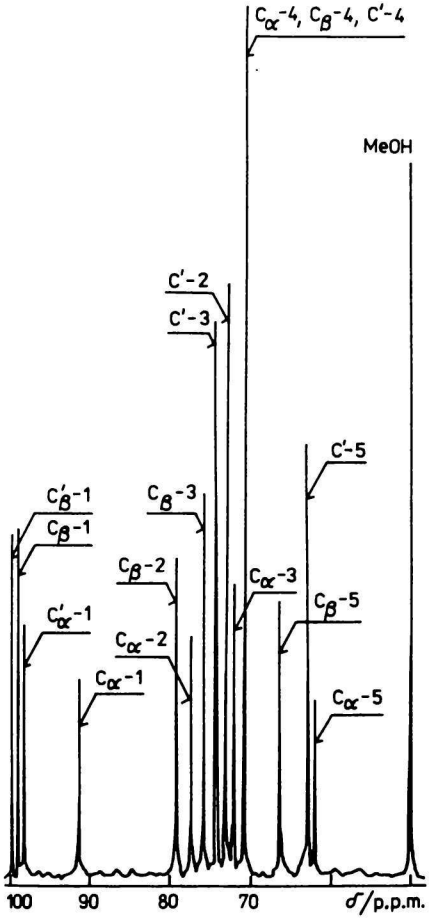


Fig. 1. ^{13}C-NMR spectrum of α-(1→2)--D-xylobiose.

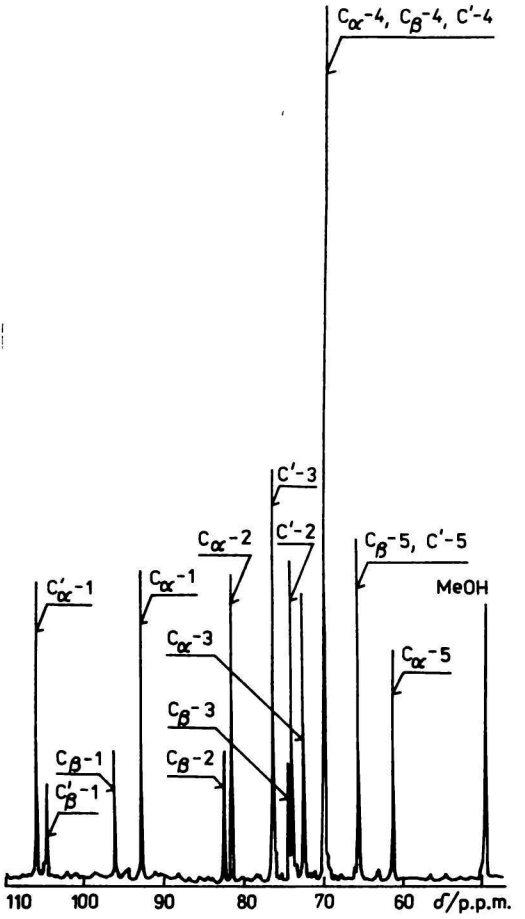


Fig. 2. ^{13}C-NMR spectrum of β-(1→2)--D-xylobiose.

99.1 p.p.m. was assigned to C-1′, the signal at 99.0 p.p.m. in the spectrum of α-(1→2)-D-xylobiose was assigned to C-1′ of the β form. Since taking into account the chemical shift and resonance intensity the signal at 90.9 p.p.m. could be unequivocally assigned to C-1 of the α form of the disaccharide, the signals at 97.8 and 98.2 p.p.m. must have originated from C-1′ of the α form and C-1 of the β form. As it was clear from the intensity of C-5 signals that the β anomer preponderates in the mixture, and because the signal at 98.2 was of almost the same intensity as that assigned to C-1′ of the β form (at 99.0 p.p.m.), the signal at 98.2 p.p.m. must have been due to C-1 of the β form and that at 97.8 p.p.m. due to C-1′ of the α form of the disaccharide. The assignment of lines in the anomeric region of the spectrum of 2-*O*-β-D-xylopyranosyl-D-xylose was easier. The more abundant α anomer (Fig. 2) was clearly recognized from the intensity of signals at 93.1 and 96.5 p.p.m. which were, thus, assigned to C-1 of the α and β form, respectively. From the intensity of signals at 105.9 and 104.9 p.p.m. follows beyond any doubt that these signals are, respectively, associated with C-1′ of the α and β form of the disaccharide.

The resonances of carbon atoms of the reducing unit of the studied disaccharides appeared as doublets reflecting the α, β anomeric ratio, which was not 1 : 1 in either case. This facilitated the assignment of signals to carbon atoms of the individual anomeric forms.

Experimental

Melting points were determined on a Kofler hot stage. Optical rotations (22°C, *c* 1) were measured with a Perkin—Elmer Model 141 automatic polarimeter. The ^{13}C-n.m.r. spectra for solution in D_2O (internal standard methanol, δ_{TMS} 50.15 p.p.m.) or $CDCl_3$ (internal standard TMS) were recorded with Jeol JNM FX-60 spectrometer. The spectra were measured at a repetition time of 2 s, pulse width of 4 μs (45°), sweep width 4000 Hz and 8 K real data points.

The studied methyl ethers of D-xylose were prepared according to standard procedures [10]; 4-*O*-methyl D-xylose, known hitherto only as a sirup, crystallized on standing and, after recrystallization from ethanol—acetone, melted at 110—117°C (anomeric mixture or anomerization during heating), $[\alpha]_D^{22} = +5.3°$ (water, equil. value after 24 h). Ref. [12] gives $[\alpha]_D^{22} = +9 \pm 2°$, for amorphous substance prepared *via* the same reaction pathway. Methyl 2-*O*-methyl-β-D-xylopyranoside (m.p. 110—112°C, Ref. [3] gives m.p. 110—111°C) was prepared by methylation of methyl 3,4-di-*O*-benzyl-β-D-xylopyranoside [14], followed by cleavage of benzyl groups by hydrogenolysis. The syntheses of methyl mono-*O*-benzyl-β-D-xylopyranosides [15—17] as well as of (1→2)- and (1→4)-linked D-xylobioses [18—20] have been described.

Thin-layer chromatography was performed on Silica Gel G and column chromatography on Silica Gel 60 (continuous gradient elution) with *A*. benzene—acetone 9 : 1, *B*. benzene—acetone 15 : 1, *C*. benzene—acetone 12 : 1, *D*. chloroform—methanol 10 : 1,

E. chloroform—methanol 15 : 1, and *F*. chloroform—methanol 5 : 1. The purity of disaccharides was verified by chromatography on Whatman No. 1 filter paper, with *G*. ethyl acetate—acetic acid—formic acid—water 18 : 3 : 1 : 4. The components were located by spraying with a) 5% (v/v) sulfuric acid in ethanol (t.l.c.) and b) anilinium acid phthalate (p.c.), and heating. Solutions were concentrated at 40°C/2 kPa.

5-O-Benzoyl-1,2-O-isopropylidene-3-O-(2,3,4-tri-O-acetyl-α- and -β-D-xylopyranosyl)-α-D-xylofuranose

2,3,4-Tri-*O*-acetyl-α-D-xylopyranosyl bromide [21] (14 g; 41.3 mmol) was added to a mixture of 5-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-xylofuranose [22] (5.25 g; 17.9 mmol) and mercuric cyanide (5.1 g; 20.5 mmol) in acetonitrile (105 ml). The mixture was stirred and after 1/2 h t.l.c. (solvent *A*) showed complete disappearance of both starting materials. After conventional processing, chromatography on a silica gel column (solvents *B*→*C*) yielded first the α isomer (1.72 g, R_f 0.5), m.p. 192.5—193.5°C (from ethanol), $[\alpha]_D^{22} = +50.7°$ (chloroform).

For $C_{26}H_{32}O_{12}$ (552.51) calculated: 56.52% C, 5.84% H; found: 56.30% C, 6.04% H.

Eluted next was the β-linked disaccharide derivative (3.95 g, R_f 0.4, total yield 75.6%, α : β = 1 : 2.3), m.p. 132—133°C (from isopropyl alcohol), $[\alpha]_D^{22} = -80.3°$ (chloroform). Found: 56.48% C, 6.0% H.

3-O-α-D-Xylopyranosyl-D-xylose

Methanolic mol dm^{-3} sodium methoxide was added to a solution of the α isomer (3.1 g, obtained as described above) in methanol (150 ml) and the resulting, strongly alkaline solution was left at room temperature for 1/2 h. T.l.c. then showed (solvent *D*) that only 1,2-*O*-isopropylidene-3-*O*-α-D-xylopyranosyl-α-D-xylofuranose was present (R_f 0.2). The mixture was neutralized with Dowex 50 W (H^+) resin and eluted from a column of silica gel (solvent *E*→*F*), to remove methyl benzoate, and the solution of the product (1.83 g) in water (36 ml) was treated with Dowex 50 W (H^+) resin (200/400 mesh, 3.6 g) for 17 h at room temperature. T.l.c. (solvent *F*) then showed that starting material was no more present and that the title disaccharide was formed. The mixture was processed conventionally and the obtained product showed m.p. 179—180°C. Ref. [23] gives m.p. 179—180°C. Yield 1 g (66%), R_{xyl} 0.55 (solvent *G*).

3-O-β-D-Xylopyranosyl-D-xylose

Methanolic mol dm^{-3} sodium methoxide was added to strong alkalinity to a solution of 5-*O*-benzoyl-1,2-*O*-isopropylidene-3-*O*-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-α-D-xylofuranose (3.5 g) in methanol (170 ml) and the mixture was heated at 60°C for 3 h. T.l.c.

(solvent *D*) then showed that only 1,2-*O*-isopropylidene-3-*O*-(β-D-xylopyranosyl)-α-D-xylofuranose (R_f 0.2) was present. The mixture was worked up as described in the preparation of the α-linked substance to give eventually 1.1 g (65%) of crystalline title disaccharide, m.p. 185—189°C (from methanol), R_{xyl} 0.7 (solvent *G*), Ref. [23] gives m.p. 188—190°C.

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