Carbohydrate Research, 207 (1990) 121–125
Elsevier Science Publishers B.V., Amsterdam

Note

Infrared spectra of the positional isomers of the methyl xylobiosides in the "anomeric region"

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(Received October 26th, 1989; accepted for publication, March 9th, 1990)

Interest in the i.r spectra of carbohydrates has been focused on hexopyranoses and their derivatives[1–6]. The important role played by the anomeric centre has been demonstrated, but little information about xylan structures has been obtained.

We have studied the (1→2)- (**2α** and **2β**), (1→3)- (**3α** and **3β**), and (1→4)-linked (**4α** and **4β**) forms of methyl *O*-α- and -β-D-xylopyranosyl-β-D-xylopyranoside in order to obtain i.r. data about the type and position of the glycosidic linkages. The determination of these molecular features is based on studies of the "anomeric region" of the i.r. spectra. The data for the methyl biosides are compared with those for α-D-xylopyranose[7], and methyl α- (**1α**) (ref. 7) and β-D-xylopyranoside[8] (**1β**). Because the frequencies of the vibrational modes depend on the physical state of the material, spectra were obtained for the crystalline and freeze-dried forms. The characteristic frequencies in the "anomeric region" (700–950 cm^{-1}) are summarised in Table I. Usually, the differences in the i.r. spectra in the anomeric region for monosaccharides[9–12] persist in oligo- and poly-saccharides and their derivatives, so that the method can be used to identify the type or position of the glycosidic linkages[9,13].

The three principal bands related to antisymmetric ring vibration (type 1), symmetric ring vibration (type 3), and glycosidic C–H deformation (type 2a for α anomers, type 2b for β anomers) are not characteristic for D-xylopyranoses[9]. Barker *et al.*[10] reported bands for the α anomer of the sugar and its glycosides at 760 and 740 cm^{-1}, respectively. The β anomers did not give these bands. There are bands near 935 cm^{-1} for pento- and hexo-pyranoses with different intensities for the α and β anomers[10]. The results for methyl α-D-xylopyranoside (**1α**) and α-D-xylopyranose in the crystalline state accord with published data, in showing three bands at 940 (type 1), 897 (type 2), and 740 cm^{-1} (type 3). Methyl β-D-xylopyranoside (**1β**) shows only one band in this region at 898 cm^{-1}. The same bands can be seen in freeze-dried materials. Therefore, the type 2a and 2b bands are not characteristic for xylopyranose derivatives. The type 1 and 3 bands are more pronounced in the α anomer and they are characteristic of the type of linkage in the studied models (Table I) as expected. Thus, the type of glycosidic linkage can be determined unambiguously from the presence in the α anomers, or absence from the β

0008-6215/90/$ 03.50

TABLE I

I. r. bands of α-D-xylopyranose, methyl α- and β-D-xylopyranoside, and methyl xylobiosides in the anomeric region (950–700 cm^{-1})

Compound	*Physical state*[a]	*Frequencies* (cm^{-1})[b]					*M.p.*(°)	*Ref.*
α-D-Xyl*p*								
	C	930s		900s		750s		7
	FD	934m		890m		750m		7
α-D-Xyl*p*-OMe (**1α**)								
	C	942s		897m		742m		8
	FD	934s		897m		734m		
β-D-Xyl*p*-OMe (**1β**)								
	C			898s				
	FD			897s				
α-D-Xyl*p*-(1→2)-β-D-Xyl*p*-OMe (**2α**)								
	C	935s	918w	902s	880s	765s	183–184	
	FD	934s	917m	902w	897s	764m		
α-D-Xyl*p*-(1→3)-β-D-Xyl*p*-OMe (**3α**)								
	C		919w	900s			195–196	
	FD	933m	913w	899m	774m	764m		
α-D-Xyl*p*-(1→4)-β-D-Xyl*p*-OMe (**4α**)								
	C	943s	909sh	893s		768s	147–149	
	FD	934m		895m		769m		
β-D-Xyl*p*-(1→2)-β-D-Xyl*p*-OMe (**2β**)								
	C			898m	886s		155–157	
	FD			897m	885w			
β-D-Xyl*p*-(1→3)-β-D-Xyl*p*-OMe ($\mathbf{3\beta_1}$)								
	C			904s			163–164	
	FD			897m				
β-D-Xyl*p*-(1→3)-β-D-Xyl*p*-OMe ($\mathbf{3\beta_2}$)								
	C		920m		885m		87–95	
	FD			902w				
β-D-Xyl*p*-(1→4)-β-D-Xyl*p*-OMe ($\mathbf{4\beta_1}$)								
	C			902m	888m		171–172	
	FD			897m				
β-D-Xyl*p*-(1→4)-β-D-Xyl*p*-OMe ($\mathbf{4\beta_2}$)								
	C			897s			91–92	
	FD			897m				

[a] Key: C, crystalline; FD, freeze-dried. [b] Key: s, strong; m, medium; w, weak; sh, shoulder.

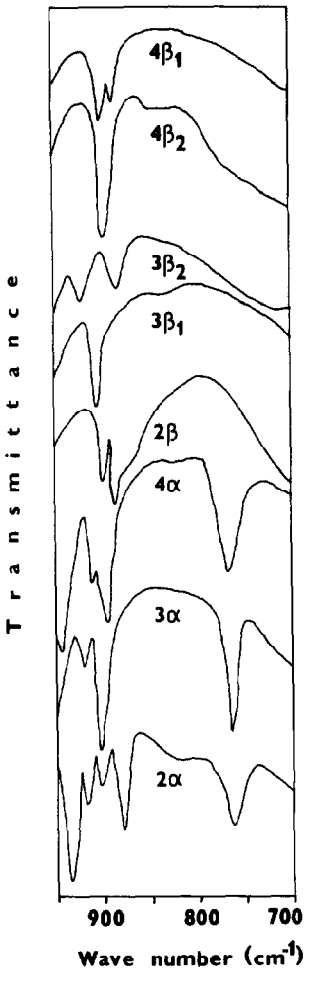

Fig. 1. I.r. spectra of crystalline methyl xylobiosides.

anomers, of these two types of i.r. band. The position of the vibrational mode at 760 $\pm 15\ cm^{-1}$ for the α-linked biosides (**2α–4α**) is shifted toward higher frequencies (by 25 cm^{-1}) in comparison with the monomers (Table I). The freeze-dried form of **3α** showed a doublet. In addition to the antisymmetric ring vibration, several peaks of medium intensity at 909–920 cm^{-1} were present in the spectra of α-linked biosides, the positions of which were not affected by the physical state (Fig. 1).

Whereas the type 2a band, normally used to distinguish between anomers, is absent from the spectra of α-D-xylopyranose and its derivatives, the type 2b band at 897 $\pm 7\ cm^{-1}$ is given by both α- and β-D-xylopyranose and their derivatives, a phenomenon[1] that remains to be explained. The type 2b band, which mainly characterises the C-1–H deformation vibration of β-hexopyranoses was found in the i.r. spectrum of each of the compounds studied, but there were differences in the position, shape, and relative intensities (Fig. 1 and Table I).

For the α-linked biosides (**2α**–**4α**), there was a shift of the main ν_{max} toward higher frequencies (**2α**, 880 cm^{-1}; **4α**, 893 cm^{-1}; **3α**, 900 cm^{-1}). In the β-series, the identification was complicated by the existence of crystallographic modifications (**3β**$_1$ and **3β**$_2$; **4β**$_1$, **4β**$_2$, and **4β**$_3$), the melting points of which are given in Table I. The polymorphs **4β**$_3$ (m.p. 148–149°) and **4β**$_2$ (m.p. 90–92°) gave identical i.r. spectra. The most intense peaks were at 903 cm^{-1}, for **3β**$_1$ and **4β**$_1$, and 897 cm^{-1} for **4β**$_2$. There were bands of medium intensity at 920 and 885 cm^{-1} (for **3β**$_2$), 902 and 888 cm^{-1} (for **4β**$_1$), and 898 and 886 cm^{-1} (for **2β**). According to a theoretical study of α- and β-D-glucose[3,4], the vibrational modes are highly coupled in the "anomeric region". For the xylobiosides, there are assignments of experimental data which are not in satisfactory agreement with the description of the vibrational modes of the C-1–H group. In addition to the band at 899 cm^{-1}, related to the C-1–H vibration, there is an antisymmetric ring vibration at 887 ± 2 cm^{-1} in the spectra of **2α**, **2β**, **3β**$_2$, and **4β**$_1$. Another vibration can be seen at 915 ± 5 cm^{-1} in the spectra of the α-biosides and **3β**$_2$. The pyranose ring vibrations below 885 cm^{-1} were not detected in the spectra of the xylobiosides. On the basis of the comparison of the i.r. spectra of crystalline methyl biosides with the model monomer compounds, it is concluded that peaks at 920, 904, 897, and 887 cm^{-1} belong to vibrations of the pyranose ring, but it is not excluded that the band at 898 cm^{-1} is the deformation band of the C-1–H group.

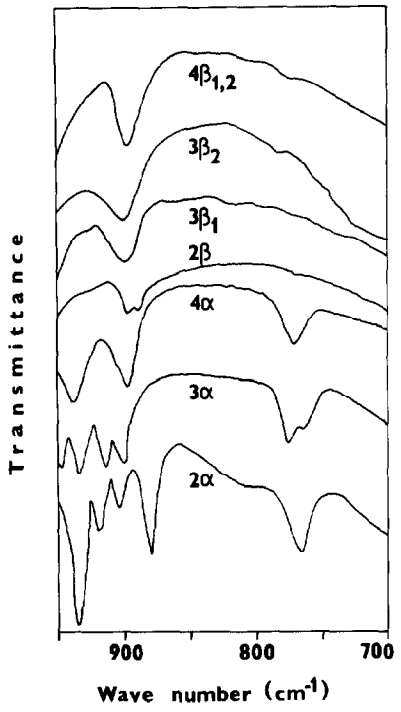

Fig. 2. I.r. spectra of freeze-dried methyl xylobiosides.

No systematic differences between the α- and β-biosides in Table I, with respect to the position of linkages, were observed. There were distinct differences between the spectra of the freeze-dried and crystalline samples. For the α-biosides, the position of the band at 898 ± 4 cm^{-1} and the ring vibrations (except for **3α** where there was one additional vibration at 900 cm^{-1}) are at the same frequency regardless of the physical state of the sample (Figs. 1 and 2). There were significant differences in the β series. The spectra of freeze-dried samples were diffuse and of typical shape for amorphous materials. The type 2 band (899 ± 2 cm^{-1}) was present in the i.r. spectrum of the β-bioside and in that of methyl β-D-xylopyranoside.

Thus, i.r. spectra in the "anomeric region" are suitable for the identification of the type and position of the glycosidic linkages in the crystalline xylobiosides, whereas those of the freeze-dried form give information only about the anomeric configuration.

EXPERIMENTAL

The i.r. spectra were recorded with a Perkin–Elmer G 983 spectrophotometer, using the standard KBr technique (1:100 mg sample:KBr) for crystalline and freeze-dried materials. The spectra were recorded at a resolution of 3 cm^{-1}. The methyl D-xylopyranosides and α-D-xylopyranose (products of LACHEMA, Czechoslovakia) and methyl xylobiosides[14] were used without purification.

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