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FT-IR study of plant cell wall model compounds: pectic polysaccharides and hemicelluloses

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Abstract

Pectic polysaccharides and hemicelluloses extracted from plants were studied in highly hydrated films on BaF_2 discs. Distinctive absorption band maxima in the mid-infrared region at 1200–800 cm^{-1} were shown to be useful for the identification of polysaccharides with different structure and composition. Two series of the hexopyranose and pentopyranose monosaccharides, which are the structural units of the plant cell wall polysaccharides, were also studied by FT-IR spectroscopy in solution (i.e. comparable to the amorphous state of the polymers). Their spectral data showed that the main IR band positions are influenced by the relative position of axial and equatorial (OH) groups on the pyranoid ring.

Keywords: FT-IR spectroscopy; Cell wall; Polysaccharides; Monosaccharides

1. Introduction

The plant cell wall is a dynamic and highly ordered complex of biopolymers containing homo- and structurally related heteroglycans (Aspinall, 1983; Brett & Waldron, 1996) in various contents, depending on the development, age and type of the cell wall. Three principally independent but interacting networks that form local microdomains can be distinguished: cellulose–hemicelluloses, pectins, and structural cell wall proteins (Schindler, 1998).

Infrared spectroscopy is quite extensively applied in plant cell wall analysis (Kačuráková & Wilson, 2000). FT-IR microspectroscopy allows monitoring of developmental and compositional changes in cell walls, and 2D FT-IR studies the mechanical properties and biopolymer interactions (Chen, Wilson & McCann, 1997; McCann, Hammouri, Wilson, Belton & Roberts, 1992; Noda, Dowrey & Marcott, 1999). These new applications require model data that allow in muro identification of particular polysaccharides present in the complicated network of the cell wall.

Cellulose and pectin (Cael, Gardner, Koenig & Blackwell, 1975; Chen et al., 1997; McCann et al., 1992; Sun & Hughes, 1999, 1998; Wellner, Kačuráková, Malovîková, Wilson & Belton, 1998) were the most extensively studied polysaccharides by IR spectroscopy. Pectins include polysaccharides of complex structure where the linear backbone is built up of (1 → 4)-linked α-D-galacturonan with regions of alternating (1 → 4)-α-D-galacturonic acid and (1 → 2)-α-L-rhamnopyranosyl residues. To the ramified regions are covalently bound neutral fractions of arabinose and galactose residues creating heteropolysaccharide complexes of rhamnogalacturonan with arabinans, galactans, and arabinogalactans. The hemicelluloses include xyloglucans, xylans, glucomannans and galactoglucomannans. Despite the great involvement of diverse pectic polysaccharides and hemicelluloses in the cell wall, they were not particularly studied by means of FT-IR spectroscopy, except for the xylans (Coimbra, Barros, Barros, Rutledge & Delgadillo, 1999; Kačuráková, Ebringerová, Hirsch & Hromádková, 1994; Kačuráková, Belton, Wilson, Hirsch & Ebringerová, 1998; Kačuráková, Wellner, Ebringerová, Wilson & Belton, 1999; Sun, Fang, Goodwin, Lawther & Bolton, 1998a,b; Sun, Fang, Rowlands & Bolton, 1998). The ability to analyze the structure of the cell wall networks is still impeded by a lack of suitable models. Utilizing further available polysaccharide models we now report FT-IR applied to the hemicellulose and pectin family polysaccharides which commonly occur in many higher plant cell walls.

In order to identify the particular polysaccharides we used infrared data of model compounds representing individual polysaccharide types and their mixtures, based on major sugar components. The role of (COH) side groups in ring

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Table 1
The structure and composition of studied plant cell wall polysaccharides

No	Compound	Structure		Neutral sugar composition (molar fractions in %)						Uronic acids (wt. %)		Plant source (references)
		Backbone	Side-chains	Rha	Ara	Xyl	Man	Glc	Gal	GalA	GLcA	
1	Pectin	α-(1 → 4)-Gal*p*A + RhaGalUA-**I**	α-Araf-β-(1 → 4,5)-Galp_n, α-(1 → 3,5)Araf_n	4.2[a]	51.9	2.1	1.3	9.7	30.0	66.2		Hawthorn (berries) (Ebringerová & Košíková, 1993)
2	Rhamnogalacturonan	α-(1 → 4)-Gal*p*A branched at O-3 α-(1 → 2)-Rha*p* branched at O-4	β-GlcA β-(1 → 4)-Gal*p*	43.2					56.8	25.3	25.3	*Althaea officialis* L. (roots) (Capek, Rosík, Kardošová & Toman, 1987)
3	Galactan	β-(1 → 6)-Gal*p*							100			*Malva manuritiana* L. (flowers) (Capek & Kardošová, 1995)
4	Arabinan	α-(1 → 5)-Ara*f* branched at O-2 or O-3	α-Ara*f*		100							*Althaea officialis* L. (roots) (Capek, Toman, Kardošová & Rosík, 1983)
5	Arabinogalactan	β-(1 → 6)-Gal*p* branched at O-3	α-Ara*f* α-(1 → 5)-Araf_n,		53.8				46.2			*Malva mauritiana* L. (flowers) (Capek, 1995)
6	Arabinogalactan	β-(1 → 3)-Gal*p* branched at O-6	α-Ara*p*, α-(1 → 3)-Araf_n, β-Galp, β-(1 → 6)-Galp		7.7				92.3			*Larix sibirica* L. (wood) (Karácsonyi, Kovácik, Alfoldi & Kubacková, 1984)
7	Arabinogalactan (Type **II**)	β-(1 → 3)-Gal*p* branched at O-6	β-(1 → 6)-Galp_n, α-Ara*f*, α-(1 → 5)-Araf_n	0.2	12.5	1.2	–	–	85.9	0.05		*Larix dahurica* L. (wood) (Odonmazig, Ebringerová, Machova & Alfoldi, 1994)
8	Arbinogalactan (Type **II**) + Glucomannan (9:1, (w/w))	β-(1 → 3)-Gal*p* branched at O-6 + β-(1 → 4)-Glc*p*, β-(1 → 4)-Man*p*	β-(1 → 6)-Galp_n, α-Ara*f*, α-(1 → 5)-Araf_n	0.2	6.2	0.8	9.3	0.8	82.3	0.1		Green corree (bean) (Ebringerová, unpublished results)
9	Arabinogalacto-rhamnoglycan	β-(1 → 6)-Gal*p* branched at O-3 α-(1 → 4)-Rha*p*	α-Ara*f*, α-(1 → 5)-Ara*f*	42.3	34.3				23.4			*Malva mauritiana* L. (flowers) (Capek, Kardošová & Lath, 1999)
10	Xyloglucan	β-(1 → 4)-Glc*p* branched at O-6	α-Xyl*p*, α-(1 → 2)-Xyl*p*, terminal β-(1 → 2)-Gal*p*, α-Fuc*p*[b]			42.1		41.6	9.9			*Pisum sativum* L. (Capek, unpublished results)
11	Glucan	α-(1 → 6)-Glc*p*						100				*Althaea officalis* L. (roots) (Capek, Toman, Rosík, Kardošová & Janecek, 1984)
12	Glucomannan	β-(1 → 4)-Man*p* β-(1 → 4)-Glc*p*					70.3	29.7				*Populus monilifera* L. (wood) (Kubačková, Karácsonyi & Bilisics, 1992)
13	Galactoglucomannan	β-(1 → 4)-Man*p* β-(1 → 4)-Glc*p*	α-Gal*p*				2.3	18.9	76.4			*Picea abies* Karst (wood) (Capek et al., 1998)
14	Arabinoglucuronoxylan + galactoglucomannan	β-(1 → 4)-Xyl*p* + β-(1 → 4)-Glc*p* + β-(1 → 4)-Man*p*	α-Ara*f*, α-4MeGA, α-Gal*p*	–	18.5	58.3	13.8	7.5	1.9	13.8[c]		Spruce wood (pulp) (Ebringerová, Banzragch, Malovíková & Kačuráková, 1993)

[a] Contains 0.7 mol% fucose.
[b] Contains 6.4 mol% fucose.
[c] 4-O-methylglucuronic acid.

vibrations was verified with monosaccharide models measured in aqueous solutions, which represent structural moieties of the polysaccharides.

2. Methods

2.1. Materials

The polysaccharides studied, their structural features determined by NMR and methylation analysis, and origin are listed and referenced in Table 1. The polysaccharide model compounds were isolated and purified as indicated in published references in Table 1 from various plant materials. An AG/mannan fraction (sample **8**) was prepared from green coffee beans according to Bradbury and Hallifay (1990). The classification of polysaccharides given in Table 1 was done according to their occurrence in plant cell walls (Aspinall, 1983; Brett & Waldron, 1996).

The eight monosaccharide model compounds (D-glucose, D-mannose, D-galactose, D-talose, D-xylose, D-lyxose, D-arabinose, and D-ribose) were produced and kindly provided by the Institute of Chemistry's manufacture unit, SAS, Bratislava.

2.2. FT-IR spectroscopy

Infrared spectra were measured on a NICOLET Magna 750 spectrometer with DTGS detector and OMNIC 3.2 software. 128 scans at a resolution of 4 cm^{-1} were averaged. As plant cell walls contain hydrated biopolymer networks, we measured highly hydrated polymer films. These were prepared by drying from 0.5% (w/v) aqueous solution on a BaF_2 window. Dry films were then hydrated by exposure to an atmosphere of fixed relative humidity (RH) above saturated solutions of NaCl (76% RH) and $NaSO_4$ (93% RH) at room temperature (Chen et al., 1997; Kačuráková et al., 1998). No significant spectral differences were found between the infrared spectra of samples measured at 76 and 93% RH, except for sample **13**. The BaF_2 background was subtracted from the spectra.

The monosaccharides were measured in 5% (w/w) aqueous solutions using a BaF_2 transmission cell with a 25 μm teflon spacer. 128 scans at 4 cm^{-1} resolution were coadded and referenced against water.

3. Results and discussion

The analysis of FT-IR data showed that each particular polysaccharide has a specific band maximum in the 1200–1000 cm^{-1} region shown in Table 2. This region is dominated by ring vibrations overlapped with stretching vibrations of (C–OH) side groups and the (C–O–C) glycosidic bond vibration.

3.1. Pectic polysaccharides

In the pectin and rhamnogalacturonan mixture (**1**) the earlier assigned pectin (**I**, Table 2) bands at 1100 and 1017 cm^{-1} were strongest (Fig. 1a), similarly as reported earlier (Coimbra et al., 1999; Wellner et al., 1998). The unique spectral shape of pectin is due to the high homogalacturonan content. In the case of rhamnogalacturonan the band shape is different with the main maximum at about 1070 cm^{-1}. The rhamnogalacturonan (**2**) maxima (Fig. 1a) were at 1070 and 1043 cm^{-1}. Both samples **1** and **2** have α-linked backbones. However, a band at 1072 cm^{-1} was also specific for β-galactan (**3**) (Fig. 1a). Thus we assigned the dominant absorbance maximum in compounds **2** and **3** to the galactose unit, irrespective of the type of glycosidic link.

In the case of α-linked arabinan (**4**) the IR maximum was at 1039 cm^{-1} (Fig. 1b). The β-arabinogalactans had two bands, sample **5** at about 1074 and 1045 cm^{-1} and samples **6** and **7** at 1078 and 1043 cm^{-1} (Fig. 1b and c). These two bands may belong to their particular components; the former to galactopyranose in the backbone and the latter to arabinofuranose units in side branches. Their relative IR absorption intensities vary with the relative amounts in the two *Larix* samples **6** and **7**, which differ in side chains. The higher amount of galactose units in sample **6** is reflected in the spectrum by the intense galactose-related maximum. The band at 1066 cm^{-1} in sample **8** (Fig. 1c), arises from the mannopyranose component. In arabinogalactorhamnoglycan (**9**) which has a band maximum at 1049 cm^{-1}, the arabinofuranose and rhamnopyranose dominate over the galactopyranose units (Fig. 1c). It is similar to the band that was found in sample **2**. In order to verify that this is the contribution of the rhamnose unit, we measured rhamnopyranoside (not shown) whose maximum was found at 1055 cm^{-1}.

3.2. Hemicelluloses

Hemicelluloses are another important group of plant cell wall polysaccharides. The linear and branched (1 → 4)-β-xylans such as glucuronoxylan (**II**, Table 2) and arabinoxylans show the main band maximum at about 1047 cm^{-1} (Kačuráková et al., 1994, 1998). We found the xyloglucan (**10**) (Fig. 1d) maximum at 1041 cm^{-1}, a band position which is closer to α-glucan (**11**) than to cellulose (Marchessault & Sundararajan, 1983). However, the xylan units may also influence the frequency of the IR band maximum. The band shape is influenced by the galactan from the side chain, which has a band at 1078 cm^{-1}. The α-glucan (**11**) main IR absorption bands can be found at 1041 and 1026 cm^{-1} (Fig. 1d), similar to starch (**III**; Table 2; Wilson & Belton, 1988). The glucomannan (**12**) shows in addition to the 1034 cm^{-1} glucan band a further band at 1064 cm^{-1} due to the mannose units, but we cannot explain yet the origin of the 1092 band (Fig. 1d). The galactoglucomannan (**13**) was the only sample of the studied series which showed

Table 2
FT-IR frequencies of the studied plant cell wall polysaccharides (vs, very strong, s, strong, IR band intensity; spectral data of compounds **I–IV** are taken from the literature)

No	Compound	(C–OH), (C–O–C), (C–C), ring				(Cl–H), ring				
1	Pectin	1144s	1100vs		1047, 1017vs	953	896		857	835
2	Rhamnogalacturonan	1150	1122	1070vs	1043vs, 989s	951, 916	902		846	823
3	Galactan	1155	1134	1072vs	1038vs		893	883		
4	Arabinan	1141	1097	1070	1039vs	918	895			807
5	Arabinogalactan			1074vs	1045vs		897	868		808
6	Arabinogalactan	1139		1078vs	1043, 985			880	842	
7	Arabinogalactan (Type **II**)	1156		1078vs	1040	916	892	879		
8	Arabinogalactan (Type **II**) + Glucomannan (9:1, (w/w)	1146		1066vs	1034		896	872		809
9	Arabinogalactorhamnoglycan				1049vs	914			837	810
10	Xyloglucan	1153	1118	1078vs	1041vs	945	897			
11	Glucan	1151	1104sh	1076sh	1041vs, 1026vs	916			840	
12	Glucomannan	1150		1092vs, 1064vs	1034vs	941	898	872		814
13	Galactoglucomannan	1149		1064[a]	1034vs, 960	934	897	872		813
14	Arabinoglucuronoxylan + Galactoglucomannan	1161, 1151	1109	1070	1038vs		898	881		809
I	Pectin	1152	1004vs	1082, 1051	1022vs, 972		891		834	
II	GX	1147		1084	1047vs, 985		897			
III	Starch	1155	1110	1082	1026vs	931			850	
IV	Cellulose	1162	1120		1059vs, 1033vs	930	898			

[a] Band appears at 76%RH.

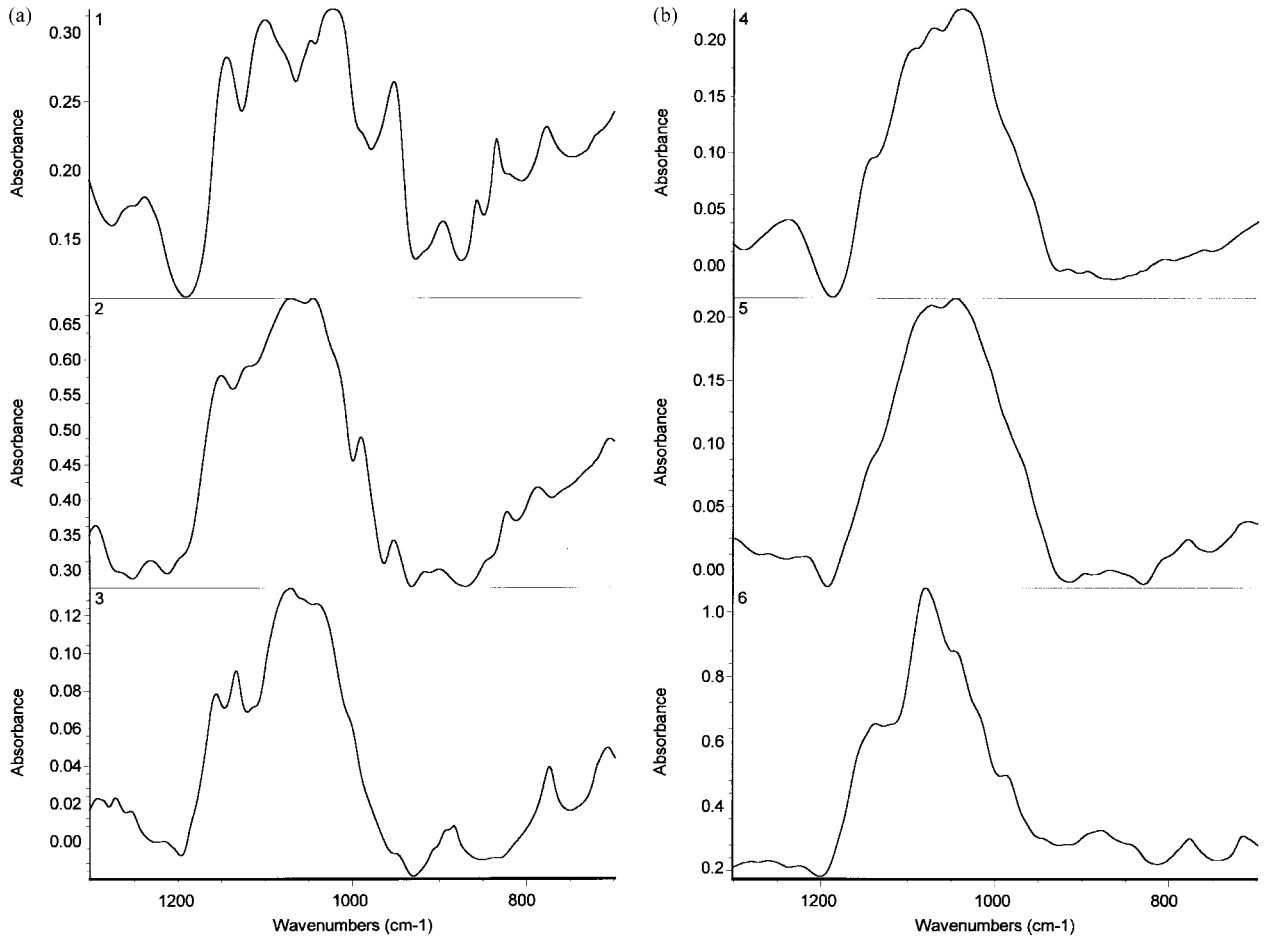


Fig. 1. FT-IR spectra of cell wall polysaccharide models in hydrated film: (a) pectin (**1**), rhamnogalacturonan (**2**), β-galactan (**3**); (b) α-arabinan (**4**), arabinogalactan (**5**), arabinogalactan (**6**); (c) arabinogalactan (type II) (**7**), arabinogalactan (type II) + mannan (**8**), arabinogalactorhamnoglycan (**9**); (d) xyloglucan (**10**), α-glucan (**11**), glucomannan (**12**); (e) galactoglucomannan (**13**), arabinoglucuronoxylan + galactoglucomannan (**14**).

different spectral shapes at 76 and 93% RH (Fig. 1e). At the higher hydration level there was only one dominant band at 1034 cm^{-1} from glucan, but at lower hydration the mannan band at 1064 cm^{-1} was also visible. The band maximum is at 1038 cm^{-1} in galactoglucomannan mixtures with arabinoglucuronoxylan (**14**) (Fig. 1e).

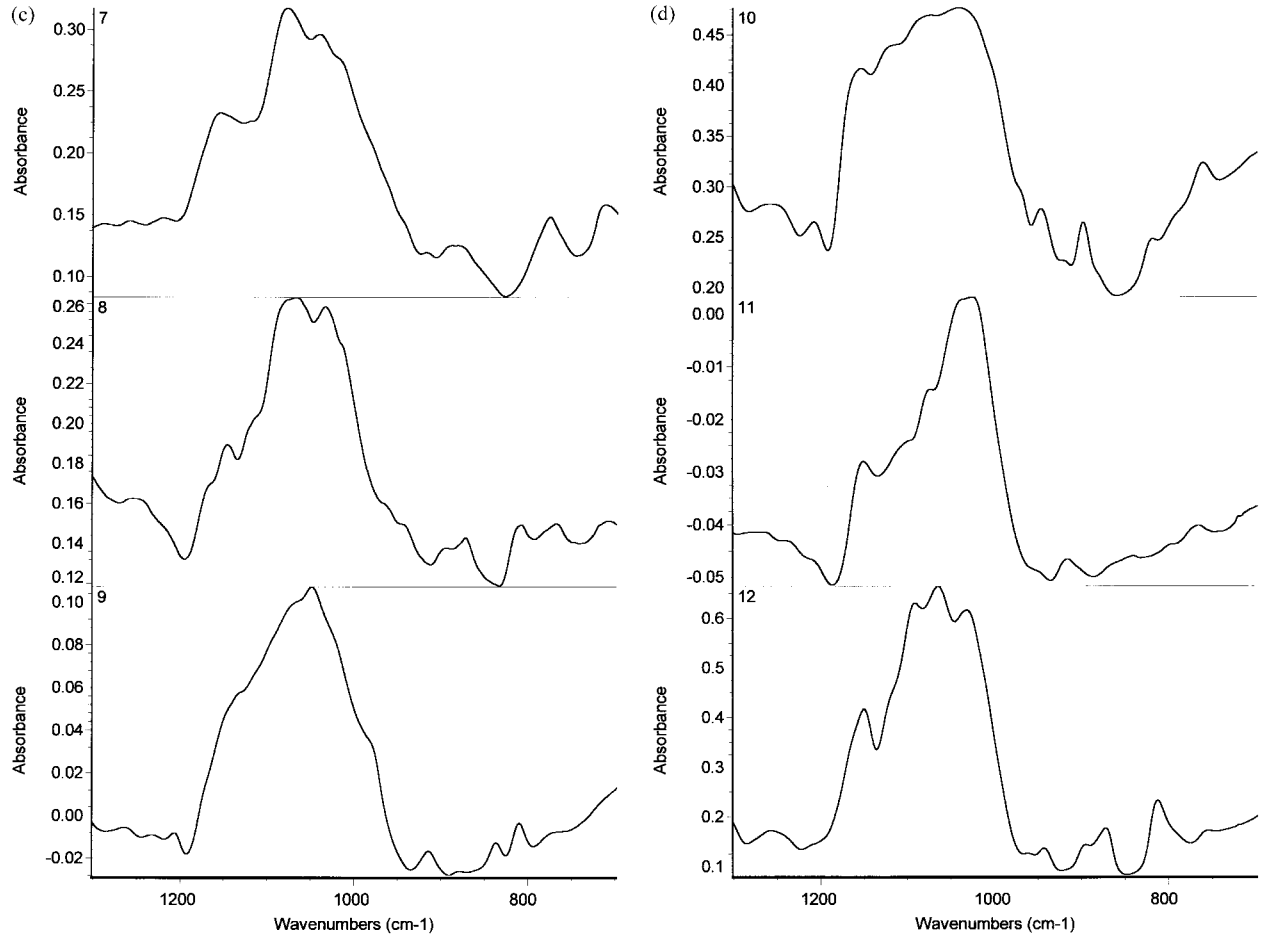
3.3. Glycosidic linkage

The IR bands at about 1160–30 cm^{-1} are dominated by the glycosidic linkage ν(C–O–C) contribution (Table 2). The highest frequency position was found for the mixed polysaccharide sample **14** at 1161 and 1151 cm^{-1}. The doublet is due to the β-(1 → 4)-glucan (cellulose, **IV**; Table 2) and β-(1 → 4) xylan units as described in the literature (Kačuráková & Wilson, 2000; Kačuráková et al., 1999; Mathlouthi & Koenig, 1986). Galactose units with any link type and position were found at about 1155 cm^{-1}, xyloglucan at 1153 cm^{-1}, and at lower frequencies (1051–1039 cm^{-1}) were polysaccharides with mannose, arabinose and rhamnose constituents.

The spectral shape with diminished bands at about 1150 and 1000 cm^{-1} was specific for the samples **4**, **5** and **9**. This phenomenon has been described earlier for (1 → 4)-xylans (Kacuráková et al., 1994, 1999) whose spectra depended on the degree of substitution and position of the substituent. Similar to the xylans our samples **4**, **5**, and **9** contained the branching point at C3 position and quite likely the spectral shape is due to this conformation which causes significant steric interaction between the arabinose side chain and the backbone.

3.4. Anomeric region

The anomeric region is complicated by band overlap, however, the bands can be unique for each sugar constituent and can give additional information to the above described region at 1200–1000 cm^{-1} (Table 2). The characteristic "anomeric region" absorption bands for α-linkage (834 cm^{-1}) and β-linkage (898 cm^{-1}) distinguish well between the two glycosidic linkage types of the aldopyranoses and the furanoid compounds at 879 and 858 cm^{-1} in carbohydrates (Mathlouthi & Koenig, 1986; Zhbankov, Adrianov & Marchewka, 1997). However, the region



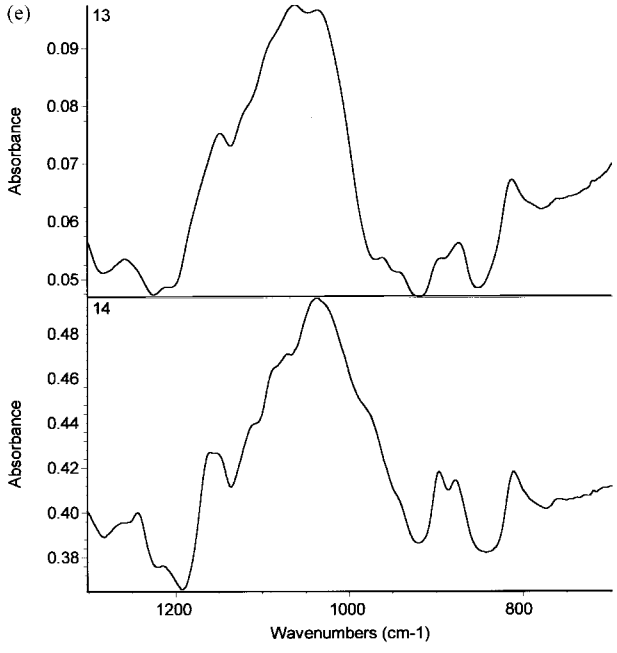


Fig. 1. (*continued*)

Table 3
Monosaccharide FT-IR frequencies (cm^{-1}) of ring and side group (COH) vibrational modes measured in 5% (w/w) aqueous solution (Hexopyranoses: Glc, glucose; Man, mannose, Gal, galactose; Tal, talsoe. Pentopyranoses: Xyl, xylose; Lyx, lyxose; Ara, arabinose; Rib, ribose)

Configuration[a]		ν(C–O–C)	Ring and side group vibrations (C–C), (C–OH), (C–H)					
Glc	C2C3C4	1149	1106		1079	**1035**		994
Xyl	C2C3C4	1156	1114	1089		**1050**	1019	980
Man	*C*2C3C4	1168			**1070**	1033	1011	
Lyx	*C*2C3C4	1164	1113	1090	**1078**	1049	1005	982
Gal	C2C3*C4*	1148			**1078**, 1060	1040		
Ara	C2C3*C4*	**1143**		**1086**	**1068**		**1005**	
Tal	*C*2C3*C4*		1119	**1092**		1056		990
Rib	*C*2C3*C4*	1156	1122	1090		**1046**	1010	

[a] Configuration of OH groups on the ring carbons: C, equatorial; *C*, axial position. Band intensity: main IR maxima indicated in bold.

above 1000 cm^{-1} is more convenient for studies of highly hydrated cell wall samples (Chen et al., 1997; Wellner et al., 1998).

The data shown in Table 2 provides evidence for the influence of both linkage type and position of the observed frequency. Except for arabinofuranose the structural units are present in pyranoid ring form. The most important bands are at about 898 cm^{-1} for β-anomer, and about 845 cm^{-1} for α-anomer form of the pyranoid ring. Galactose and mannose show bands at 875 and 810 cm^{-1}, arising from their monomer units. In sample **6** the side chains contain both arabinopyranose and arabinofuranose units forming disaccharide chains in contrary to the solely arabinofuranose units in **1**, **4** and **5**. In the anomeric region the 842 cm^{-1} band from **6** belongs to the α-linked arabinose pyranoid ring, while in the other samples the arabinose furanoid ring vibration is at higher frequency. In case both galactopyranose and arabinofuranose units are present they give non-resolved or overlapped bands at 868–880 cm^{-1}.

From the results described above we conclude that in polymer mixtures the main constituents could be recognized and we suggest the possible role of ring and (COH) group vibrations to the spectral shape.

3.5. Monosaccharides

Since the positions of the main band maxima of the polysaccharide films were shown to be characteristic for certain polysaccharide type we compared them to the spectra of their structural units in non-crystalline form. We measured hexopyranoses and pentopyranoses with different OH group configuration on C-2, C-3, C-4 (Table 3) and we correlated the main IR maxima positions of sugar monomers with the position of (C–OH) side group orientation on the ring. The region below 1200 cm^{-1} has previously been suggested as promising for analysis of structural conversions (Zhbankov, 1992).

The IR spectra of monosaccharides in the 1170–980 cm^{-1} region were sensitive to the axial and equatorial position of the (OH) groups which can affect quite significantly the main band positions (Table 3). Fig. 2 shows those monosaccharides which are structural units of the above studied polysaccharides. The preferred conformation of these hexopyranoses is C1. The all-equatorial (OH) group positions in glucose showed in the IR spectrum the lowest frequency maximum at 1035 cm^{-1}. Amid the pentopyranosides xylose showed one maximum at 1050 cm^{-1}. One axial (OH) group either in position C-2 or C-4 in the case of mannose and galactose gave maxima at 1070 and

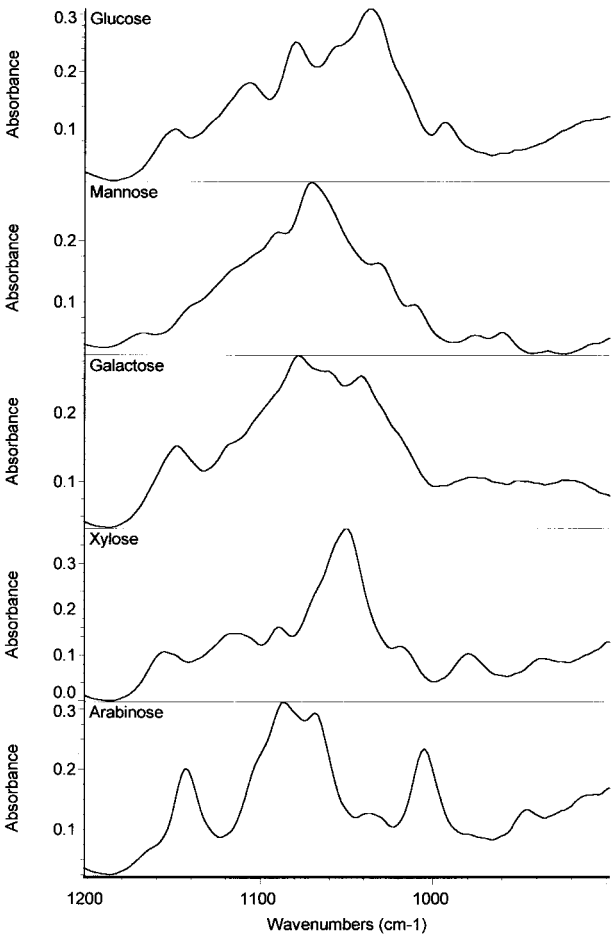


Fig. 2. FT-IR spectra of monosaccharide models measured in aqueous solution.

1078 cm^{-1}, respectively. The main IR band of lyxose was at 1078 cm^{-1}. The talose, with two (OH) groups in axial position at C-2 and C-4, had a maximum at 1092 cm^{-1}. However, arabinose showed four well-resolved high intensity bands at 1143, 1086, 1068 and 1005 cm^{-1} and ribose had one band 1046 cm^{-1}. Moreover, all pentopyranoses have a shoulder at 1090 cm^{-1}. We explain this extraordinary spectral feature with the counterbalance between the C1 and the 1C conformation. The favored conformation of the arabinose and ribose in aqueous solution (Durette & Horton, 1971) are 1C and C1–1C, respectively. The spectrum of arabinose in solution is more complicated than in arabinan, therefore we conclude that the conformation of arabinose in polymers is only C1.

The results suggest that the (C–OH) relative positions substantially influence the IR spectra by changes in their steric arrangements and interactions. We assume that the complex vibrational modes strongly reflect the ring constraint which is increasing with the number of (OH) groups in axial position. In consequence the main IR band position in the spectra of sugars and polysaccharides will be shifted towards higher frequencies, as it is the case of galactan and mannan. Having compared the hexosan and pentosan spectra of sugars with the same configuration type the (CH_2OH) group on C-6 does not show that significant influence on the spectral shape as would have been expected.

4. Conclusions

FT-IR spectra in the 1200–800 cm^{-1} region give information about the main polysaccharides present in the complicated systems of polysaccharide mixtures. The overall shape of a polysaccharide spectrum is determined by the backbone polysaccharide composition but can also be strongly influenced by the side chain constituents. At least one very intense band was identified for each particular polysaccharide structural moiety.

The IR bands of β-(1 → 6)- or β-(1 → 3)-linked galactan occur at about 1078–1072 cm^{-1}. The β-(1 → 4)-mannan was found at 1066–1064 cm^{-1}. The main chain forming arabinan was at 1039 cm^{-1} while the side chain arabinans were found at about 5 cm^{-1} higher. Xyloglucan and β-glucan showed bands at 1041 cm^{-1} while α-glucan had an additional band at 1026 cm^{-1}. Rhamnose in side chains showed a band at 1043 cm^{-1}.

These characteristic band maxima are due to the influence of the constituent monosaccharides of the studied pectic and hemicellulosic polysaccharides. Galactose showed the strongest IR band at 1078 cm^{-1}, mannose at 1070 cm^{-1}, and glucose at 1035 cm^{-1}. The relative position of axial and equatorial (OH) side groups influence the main band frequency positions at 1100–1000 cm^{-1} and the maxima assigned to ring and side group vibrations can be related to the polysaccharide spectra. Therefore, the distinctive band positions allow the identification of polysaccharide structures and their composition.

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