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INFRARED SPECTRA OF SOME O-METHYL DERIVATIVES OF GLUCOSE AND XYLOSE

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Abstract—The IR spectra (3000–670 cm^{-1}) of some O-methyl derivatives of glucose, xylose and related glycosides are reported for samples in dilute solution in inert solvents and as potassium chloride discs and hexachlorobutadiene mulls. Several bands in the C—H and C—O stretching regions of the spectra of samples in solution were found to be split in the spectra of the solid state samples. Bands in the C—H bending region and in the region below 900 cm^{-1} appeared to be little affected by the changes in environment. The implications of the results for the interpretation of solid state spectra of crystalline carbohydrates are discussed.

IN STUDIES of the structure of polymer molecules by spectroscopic techniques a knowledge of the spectra of smaller molecules related to the polymer basic unit has often been most valuable. In the case of polysaccharides the utility of this approach has been demonstrated by Marchessault.[1] However, most of the spectroscopic data for compounds such as the tetrahydropyranols[2,3] and other derivatives of tetrahydropyran,[4] which serve as simple models for the higher saccharides, have been obtained by studying samples in the form of liquid films or in solution in a solvent such as carbon tetrachloride, whereas oligo- and poly-saccharides occur as solids and are insoluble in the solvents usually employed. However, many of the O-methyl derivatives of monosaccharides are solids, and are soluble in suitable solvents allowing the spectra of the samples to be obtained in both solution and in the solid state. From such spectra the effects of environmental changes can be ascertained. These effects are important since they can cause single molecular vibrations to give rise to multiple bands which show differing dichroisms when the samples are examined with polarised radiation.

The present work forms part of a program undertaken to obtain information about the secondary structure of polysaccharides from the polarised IR spectra of single crystals of oligosaccharides having the same unit cell. Liang and Marchessault[5,6] showed that the dichroisms of bands in the polarised IR spectra of cellulose I and II could yield information about their secondary structures. They found that bands in the C—H stretching and bending regions were particularly useful. These bands were also found to be useful in a determination of the structure of a new anhydro sugar alcohol.[7] In this paper the spectra of some O-methyl derivatives of glucose, xylose and related glycosides are reported and the solid state spectra are examined for evidence of environmental effects. Spectra in the OH stretching region are not reported as they have been discussed previously.[8]

Problems of interpretation of the spectra of the model compounds can sometimes arise as a result of their conformational flexibility. However, in the earlier study[8]

TABLE 1. FREQUENCIES OF C—H STRETCHING BANDS OF O-METHYL DERIVATIVES OF GLUCOPYRANOSE, XYLOPYRANOSE AND RELATED GLYCOPYRANOSIDES

Compound	State	Frequencies (cm^{-1})								
3-O-Methyl-D-xylopyranose[a]	Solid[b]		2988	2968			2916	2894		2844
2,3 Di-O-methyl-D-xylopyranose	Solid[b]		2990		2956	2940	2910	2892		2834
	Solution		2988			2934	2906			2834
2,3,4 Tri-O-methyl-D-	Solid[b]		2982		2950		2916	2894	2864	2834
xylopyranose	Solution		2984			2942		2902		2836
Methyl 2,3,4-tri-O-methyl-	Solid[b]		2976			2930	2906			2840
D-xylopyranoside	Solution		2978			2930	2906			2840
2-O-Methyl-D-glucopyranose[a]	Solid[b]		2972			2924		2900		2852
3-O-Methyl-D-glucopyranose[a]	Solid[b]	3015	2974		2948		2912	2890	2876	2848
6-O-Methyl-D-glucopyranose[a]	Solid[b]	3026	2992	2960		2930	2910	2890		2814
2,3 Di-O-methyl-D-	Solid[b]		2984		2946		2916		2860	2836
glucopyranose	Solution[c]		2982			2932			2854	2832
2,3,6 Tri-O-methyl-D-	Solid[b]		2986			2936	2908		2874	2838
glucopyranose	Solution		2986			2928		2900		2830
2,3,4,6 Tetra-O-methyl-	Solid[b]		2982			2926		2900		2828
D-glucopyranose	Solution		2986			2934		2896		2834
Methyl 4-O-methyl β-D-	Solid[d]		2992	2966		2930		2898	2878	2832
glucopyranoside	Solution		2988	2966		2932		2904	2882	2842
Methyl 4,6 di-O-methyl β-D-	Solid[d]		2992	2962			2918		2878	2846
glucopyranoside	Solution		2986	2962		2930		2898		2836
Methyl 2,3,4 tri-O-methyl	Film		2976			2922				2828
α-D-glucopyranoside	Solution		2982		2946	2926	2906	2884		2832
Methyl 2,3,4 tri-O-methyl	Solid[d]		2988			2926	2904	2880		2833
β-D-glucopyranoside	Solution		2980		2950	2928	2912	2882		2834
Methyl 2,3,4,6 tetra-O-methyl	Film		2986			2932				2834
α-D-glucopyranoside	Solution		2986			2924				2834

[a] Insoluble in solvents used

[b] Solid—Frequencies given are averages of results obtained from KCl discs and hexachlorobutadiene mulls

[c] Spectrum of low intensity owing to low solubility

[d] Disc only due to limited quantity of sample.

of a number of these compounds only in one case, that of 2,3 di-O-methyl-D-xylopyranose, did the compound appear to exist in other than the C1 conformation.[9]

The C—H stretching frequencies of the various compounds are listed in Table 1 and the spectra of 2,3 di-O-methyl-D-xylopyranose and 2,3,4 tri-methyl-D-xylopyranose obtained from samples in both dilute solution in carbon tetrachloride and in the solid state are compared in Fig. 1.

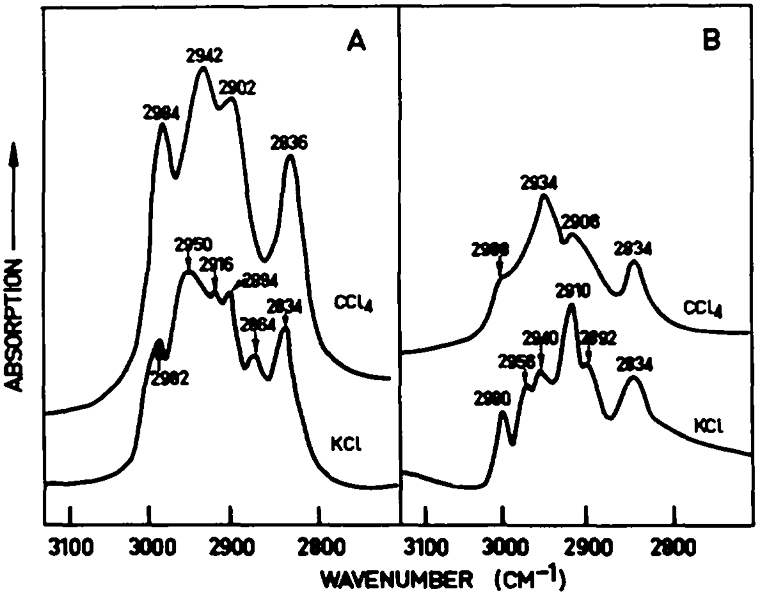

FIG. 1 Spectra in the C—H stretching region.

A. 2,3,4 tri-O-methyl-D-xylopyranose

B. 2,3 di-O-methyl-D-xylopyranose.

The spectra obtained in dilute solutions will be discussed first, as they are simpler. In the C—H stretching region, the solution spectrum of 2,3,4 tri-O-methyl-D-xylopyranose may be expected to contain bands arising from three Me groups, one methylene group at C_5 (see Ref. 3) and five methine groups. Each Me and methylene group should give rise to two bands corresponding to symmetrical and unsymmetrical vibrations of the C—H bonds. For saturated hydrocarbons intensities of the bands decrease in the order: Me unsymmetrical stretching, Me symmetrical stretching, methylene unsymmetrical stretching, methylene symmetrical stretching and methine stretching vibrations. The intensity of each is diminished when the C—H containing group is adjacent to an O atom.[10] According to Marchessault[1] the Me unsymmetrical and symmetrical stretching vibrations in OMe derivatives of tetrahydropyran absorb near 2975 and 2832 cm^{-1} respectively. Both bands are well defined in the spectra of all of the compounds. The value for the symmetrical vibration is appreciably lower than that associated with C—CH_3 groups and is in accord with the value obtained by Henbest *et al.*[11] for OMe groups in substituted cyclohexanes and steroids. Similarly in the spectra of tetrahydropyran and its derivatives the methylene unsymmetrical and symmetrical stretching vibrations have been found[1] to absorb near 2935 and 2850 cm^{-1} respectively. Marchessault[1] has not distinguished between the frequencies of the ring methylene group and those of the hydroxymethyl group, but Sohar *et al.*[7] have suggested that the C—H frequencies of a CH_2—O— group should be lower than those of a CH_2—OH group on the basis of the C—H bond near the ether–oxygen being less polarised than in the vicinity of an OH group. In most of the compounds listed in Table 1 strong absorption is evident near these frequencies but in most cases the lower frequency absorption could not be resolved from that of the Me vibration. In many cases, however, the absorption near 2935 cm^{-1} is far more intense than would seem appropriate for one or two methylene groups, so it may be that methine groups absorb here, as well as near 2910 cm^{-1} as found by Stacey, *et al.*,[12] for the group involving the anomeric C atom, and near 2890 cm^{-1} as found by Fox and Martin.[13] Another possibility is that this band may gain intensity from a resonance interaction between an overtone of a C—H bending vibration of, for example, a Me group and one of the C—H stretching vibrations. As the solution spectra of the α and β forms of methyl 2,3,4 tri-O-methyl-D-glucopyranoside are almost identical, it would seem that in this region bands associated with Me groups are relatively insensitive to the axial or equatorial orientations of the groups.

From the frequencies in Table 1 and the spectra in Fig. 1 it is clear that there are more bands in the C—H stretching region of the spectra obtained from solid state samples than from solutions. The additional bands cannot be artifacts arising from the incorporation of the samples in KCl discs since an identical spectrum is obtained from samples mulled with hexachlorobutadiene. Hornig[14] has suggested a number of ways in which a single molecular vibration can give rise to multiple bands in a crystal: (i) Through changes in the selection rules arising out of the alteration in the symmetry of the potential field. Such changes are related to the symmetry of the molecular site[15] in the crystal. (ii) Through coupling between similar vibrations in different molecules. These interactions are controlled by the symmetry of the entire unit cell. In Table 2 are shown the splitting of the bands predicted from a knowledge of the symmetry of the crystals of those compounds for which such information is available.[16] Coupling involving Me vibrations would appear to be possible, but coupling between methine stretching vibrations would seem likely to be weak in a

TABLE 2. SPLITTING OF BANDS IN THE CRYSTAL SPECTRA OF O-METHYL DERIVATIVES OF GLUCOPYRANOSE, XYLOPYRANOSE AND A RELATED GLYCOPYRANOSIDE

Compound	Space group	Molecules in unit cell	Splitting under Site symmetry	Splitting under Unit cell symmetry
2,3,4 Tri-O-methyl α-D-xylopyranose	$P2_1$	2	1	2
2,3,6 Tri-O-methyl α-D-glucopyranose	$P2_12_12$	4	2	4*
2,3,4,6 Tetra-O-methyl α-D-glucopyranose	$P2_12_12_1$	4	1	4*
Methyl 2,3,4 tri-O-methyl β-D-glucopyranoside	$P2_12_12$	4	2	4*

* One component is infrared inactive

case such as that of the α anomer of 2,3,4 tri-O-methyl-D-xylopyranose, the predominant anomer in our sample,[8] since under the operations of the space group ($P2_1$)[16] the methine vibrations are either approximately parallel or antiparallel to each other. (iii) Through the appearance of bands due to sum and difference frequencies or overtone frequencies of molecular vibrations. Such bands could be present in the spectrum of the free molecule, but would be enhanced in the crystal by the probable increase in the anharmonicity of the potential function. (iv) Through coupling of a molecular vibration with a lattice vibration. (v) Through bands resulting from sum or difference frequencies of vibrations described in iv. The first three possibilities are probably responsible for the observed band multiplicities, since the large frequency differences between molecular and lattice vibrations makes their coupling unlikely.

The frequencies of 3026 and 3015 cm^{-1} observed in the disc spectra of 3-O-methyl-D-glucose and 6-O-methyl-D-glucose probably arise from a resonance interaction between the methyl unsymmetrical stretching vibration and an overtone of a C—H bending vibration since these frequencies are appreciably higher than those normally found for C—H bonds in saturated ring systems not subject to undue strain.[10]

Other important C—H vibrations include the unsymmetrical bending vibration of the Me group and the symmetrical bending vibrations of the Me and methylene groups. In saturated hydrocarbons the first named absorbs at 1460 cm^{-1} and the other two at 1378 and 1467 cm^{-1} respectively, with the methylene symmetrical bending vibration being approximately twice as intense as the Me unsymmetrical bending mode.[10] In the spectrum of 2-methoxytetrahydropyran two bands were observed[17] at 1465 and 1450 cm^{-1}, and each of the compounds studied here shows two bands close to these frequencies. The former probably arises from the methylene symmetrical bending mode and the latter from the C—H unsymmetrical bending mode of the Me group shifted to lower frequency by the proximity of the O atom.

The absence of bands between 1445 cm^{-1} and 1400 cm^{-1} in all the glucose derivatives, except 2,3,6 tri-O-methyl-D-glucopyranose, for which only a disc spectrum has been obtained owing to its low solubility, is surprising since Liang and Marchessault[5,6] have assigned a band at 1430 cm^{-1} in the spectra of the celluloses to a methylene symmetrical bending vibration in the hydroxymethyl group. However, it may be that the frequency of this vibration is sensitive to the condition of the neighbouring O atom.

The spectra of all the compounds studied showed bands of appreciable strength in the region 1390–1370 cm^{-1}. These bands may be assigned to the C—H symmetrical bending vibration of the Me group. In substituted cyclohexanols it was found[18] that the bending frequencies of axial Me groups were slightly higher (~ 7 cm^{-1}) than those of equatorial groups. In the present work insufficient samples were available to test whether this applied to carbohydrate derivatives also.

The spectra in the region 1500–670 cm^{-1} of methyl 2,3,4 tri-O-methyl α-D-glucopyranoside and 2,3,4,6 tetra-O-methyl-D-glucopyranose (spectrum near 900 cm^{-1} suggests a preponderance of the α-anomer[8, 19]) obtained in solution and as a film or in a disc are compared with those of methyl 2,3,4,6 tetra-O-methyl α-D-glucopyranoside in Fig. 2. The bands are listed in Table 3. Hence, it would appear that a band at 1250 cm^{-1} in the solution spectrum (Fig. 2A) and a band at 1264 cm^{-1} in the disc spectrum (Fig. 2B) of 2,3,4,6 tetra-O-methyl-D-glucopyranose arise from the in-plane bending vibrations of the anomeric secondary OH group. Similarly in the spectrum of methyl 2,3,4 tri-O-methyl α-D-glucopyranoside the same vibration of the primary OH group gives rise to a band at 1227 cm^{-1} in the solution spectrum (Fig. 2E) and 1236 cm^{-1} in the disc spectrum (Fig. 2F). When the solution spectrum of 2,3,4 tri-O-methyl-D-xylopyranose is compared with that of methyl 2,3,4 tri-O-methyl-D-xylopyranoside the absorption arising from the in-plane bending mode of the anomeric secondary OH group is not so obvious but appears to overlay another band at 1260 cm^{-1}. A comparison of the disc spectra, however, does not reveal bands arising from this vibration.

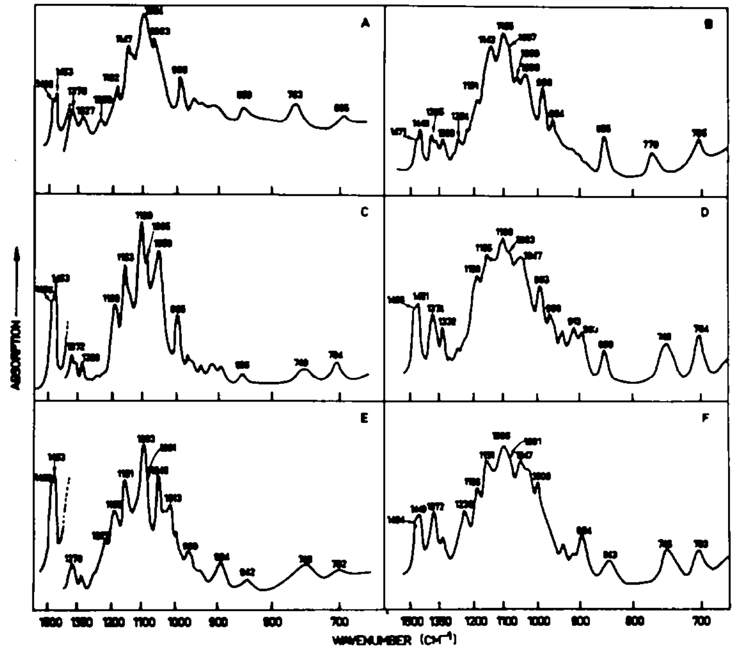

FIG. 2 Spectra in the region 1500–670 cm^{-1}.

A. 2,3,4,6 tetra-O-methyl-D-glucopyranose in solution in C_2Cl_4 and CS_2
B. 2,3,4,6 tetra-O-methyl-D-glucopyranose in a KCl disc
C. methyl 2,3,4,6 tetra-O-methyl α-D-glucopyranoside in solution in C_2Cl_4 and CS_2
D. methyl 2,3,4,6 tetra-O-methyl α-D-glucopyranoside in a film
E. methyl 2,3,4 tri-O-methyl α-D-glucopyranoside in C_2Cl_4 and CS_2
F. methyl 2,3,4 tri-O-methyl α-D-glucopyranoside in a film

The solution spectra of the three previously mentioned glucopyranose derivatives and of 2,3,4 tri-O-methyl-D-xylopyranose and methyl 2,3,4 tri-O-methyl-D-xylopyranoside appear to be very similar in the region 1190–1050 cm^{-1} with the most intense peak appearing in each case near 1095 cm^{-1}, and in the cases of methyl 2,3,4 tri-O-methyl α-D-glucopyranoside, methyl 2,3,4,6 tetra-O-methyl α-D-glucopyranoside and methyl 2,3,4 tri-O-methyl-D-xylopyranoside there are also shoulders near 1082 cm^{-1}. In view of Page's findings[20] that absorptions arising from C—O bonds in methoxy steroids could be used to characterize them as equatorial (1104–1100 cm^{-1}) or axial (1090–1086 cm^{-1}) the higher frequency absorption above could possibly be assigned to equatorial O-Me groups and the lower to axial groups. Other strong absorptions in this region, also, arise almost certainly from C—O vibrations.

In steroid and triterpenoid alcohols C—O stretching vibrations of equatorial and axial OH groups have been distinguished.[21] However, in the carbohydrate derivatives studied here the C—O stretching vibration of the alcohol groups does not appear to be clearly marked.

By analogy with the spectra of steroidal sapogenins[22] strong bands near 990 cm^{-1} probably arise from C—C stretching vibrations enhanced in intensity by their proximity to oxygenated groups. Bands near 965 cm^{-1} have, however, been assigned to terminal Me rocking vibrations.[19]

In the spectra of the glucopyranose derivatives characteristic bands which have been assigned by Barker *et al.*[19] are present near 910, 850 and 755 cm^{-1}. An additional band occurs near 700 cm^{-1}. In the xylopyranose derivatives a band at 885 cm^{-1} is prominent in both spectra and a band at 745 cm^{-1} characteristic of α-anomers[23] in the spectrum of 2,3,4 tri-O-methyl-D-xylopyranose. All these bands appear to be little affected by the state of the sample.

The spectra of films of methyl 2,3,4 tri-O-methyl α-D-glucopyranoside, methyl 2,3,4,6 tetra-O-methyl α-D-glucopyranoside and of the disc of methyl 2,3,4 tri-O-methyl-D-xylopyranoside differed little from those of the solution spectra except that bands in the region of 1190–1050 cm^{-1} were less well resolved. However, the band at 1220 cm^{-1} in the solution spectrum of 2,3,4 tri-O-methyl-D-xylopyranose (Fig. 3A) was split into two bands at 1238 and 1220 cm^{-1} in the disc spectrum (Fig. 3B) the band at 1155 cm^{-1} into two bands at 1157 and 1144 cm^{-1} and the band at 1095 cm^{-1} into two bands at 1107 and 1087 cm^{-1}. Since the molecules of 2,3,4 tri-O-methyl-D-xylopyranose occupy sites of symmetry C1, these bands cannot have arisen as a result of site group splitting in the crystal, but have arisen probably as the result of coupling of the vibrations. The splitting of bands in the disc spectrum of 2,3,4,6 tetra-O-methyl-D-glucopyranose (Fig. 2B) is not so marked except near 1045 cm^{-1}.

In conclusion, it is clear that bands arising from certain vibrations in the compounds are more sensitive than others to changes in environment. Thus a number of bands, including those arising from the bending vibrations of methyl and methylene groups, and in the region below 900 cm^{-1} appeared to be little affected by the change in environment. Such bands can be assigned when only a solid state spectrum is available and their dichroisms in a single crystal spectrum should be those predicted by means of the oriented gas approximation. Other bands, however, including some in the C—H and C—O stretching regions were split in the solid state spectra and difficult to assign. In predicting their dichroisms in single crystal spectra account would have to be taken of intermolecular interactions in this environment. The dichroisms of the C—H stretching vibrations of methine groups would be expected to be little affected since vibrations whose transition moments are almost parallel or antiparallel, as in the case of carbohydrates crystallizing in space groups such as $P2_1$, should couple only weakly. Some of the environmental effects observed in the

TABLE 3. FREQUENCIES OF ABSORPTION BANDS IN THE RANGE 1500–670 cm^{-1} IN THE SPECTRA OF DERIVATIVES OF GLUCOPYRANOSE, XYLOPYRANOSE AND RELATED GLYCOPYRANOSIDES

I	II		III		IV	V	VI		VII	VIII		IX	X	
Solid	Solid	Solution[a]	Solid	Solution[a]	Solid	Solid	Solid	Solution[a]	Solid	Film	Solution[a]	Solid	Film	Solution[a]
1471	1460	1464	1471	1466	1464	1460 (sh)	1471	1466	1471	1464 (sh)	1466	1471	1466 (sh)	1466
1451	1445	1447	1449	1449	1445	1450	1449	1453	1449 (sh)	1449	1451	1449	1451	1451
						1430 (sh)								
						1400			1408 (sh)					
1392 (sh)	1399 (sh)		1390	1395	1395 (sh)		1389		1395			1399		
1372 (s)	1379	1374	1376	1382 (sh)	1370 (sh)	1370		1376		1372	1370	1370	1374 (sh)	1372
							1361	1359 (sh)						1355 (sh)
1346 (sh)	1346			1342	1351				1351 (w)					
1332 (sh)	1333	1333	1332	1332	1323	1333	1333	1327	1321	1330	1325	1330	1332	1328
1309		1300 (w)			1311 (sh)	1316			1311			1319		
	1282		1282 (w)	1294 (w)			1282 (w)		1285 (w)				1297 (w)	1290 (w)
1266 (s)	1264 (w)	1260	1267	1274	1267	1266	1264		1261	1266 (sh)	1266 (sh)	1272	1263 (w)	1263 (w)
						1244		1250						
	1238 (w)		1232	1235					1235 (w)	1236 (s)	1227	1235		
1215 (sh)	1220 (w)	1220			1224		1227 (w)		1220					
1196			1198 (sh)	1190	1200 (sh)	1189	1191		1193	1186 (s)	1188 (s)	1190	1188 (s)	1190 (s)
	1183	1180	1183		1188			1182						
1153 (s)	1157	1155 (s)	1160 (s)	1162	1160 (s)				1163	1151 (s)	1151 (s)	1153	1155 (s)	1153 (s)
	1144					1147 (sh)	1143 (s)	1147 (s)						
		1130 (sh)			1136 (s)	1136 (s)		1134 (sh)					1134 (sh)	1138 (sh)

1120	1123 (sh)					1117 (w)			1122 (s)		1120 (sh)	1120 (s)		
1105	1107		1100	1105 (s)	1109 (w)	1101 (w)	1105 (s)		1105 (s)				1100 (s)	1100 (s)
		1095 (s)		1093 (s)				1094 (s)		1096 (s)	1093 (s)			
1078	1087 (s)		1088 (s)		1080 (s)		1087 (sh)		1087	1081 (sh)	1080 (sh)	1085 (s)	1083 (sh)	1085
1062 (s)			1065 (sh)	1065 (s)		1070	1060	1063					1064 (sh)	1066 (sh)
		1050 (s)			1056 (s)	1050 (s)			1052 (s)	1047 (s)	1048 (s)		1047 (s)	1050 (s)
	1036 (s)						1036 (sh)	1036 (sh)	1038 (sh)			1040		
	1010	1018	1015	1020 (s)	1012 (s)	1020 (sh)				1022	1013	1022		
992		985	990	992		1005 (sh)	990 (s)	990 (s)	998 (s)	1000 (s)	1000	990 (s)	993 (s)	995 (s)
975 (s)	971		976	978 (s)		965 (sh)	964		968	968	969		968	970
	953		956	954	958		952 (w)	957 (w)					960 (sh)	962
945	935 (s)	947 (s)	943 (w)	936	945 (s)	945 (s)		936	936	936	939	935	940	940
					911	910 (sh)	917 (w)	913 (w)		913 (w)	913 (w)		913	913
	900 (sh)						905 (w)	901 (w)	900					
893	894 (s)	884	890	887	888		889 (w)			894	894	896	893	893
					851 (w)	854 (s)	855 (s)	850	858	843	842	858 (w)		
													836	836
					789									
					765	763 (s)	769	763				772 (w)		
	741 (s)	745								746	746	748 (w)	749	749
					700	706	705	695		703	702		704	704

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[*] Bands measured in solution in CS_2 except in the region 1500–1400 cm^{-1} where C_2Cl_4 was used.

(s) Strong (w) Weak (sh) Shoulder

I 2,3 Di-O-methyl-D-xylopyranose
II 2,3,4 Tri-O-methyl-D-xylopyranose
III Methyl 2,3,4 tri-O-methyl-D-xylopyranoside
IV 2,3 Di-O-methyl-D-glucopyranose
V 2,3,6 Tri-O-methyl-D-glucopyranose
VI 2,3,4,6 Tetra-O-methyl-D-glucopyranose
VII Methyl-4-O-methyl β-D-glucopyranoside
VIII Methyl 2,3,4 tri-O-methyl α-D-glucopyranoside
IX Methyl 2,3,4 tri-O-methyl β-D-glucopyranoside
X Methyl 2,3,4,6 tetra-O-methyl α-D-glucopyranoside

C—H stretching region may be associated with the O-Me groups in the samples and would not be present in the spectra of the parent monosaccharides. This possibility cannot, however, be tested readily since such carbohydrate derivatives are insoluble in the appropriate solvents.

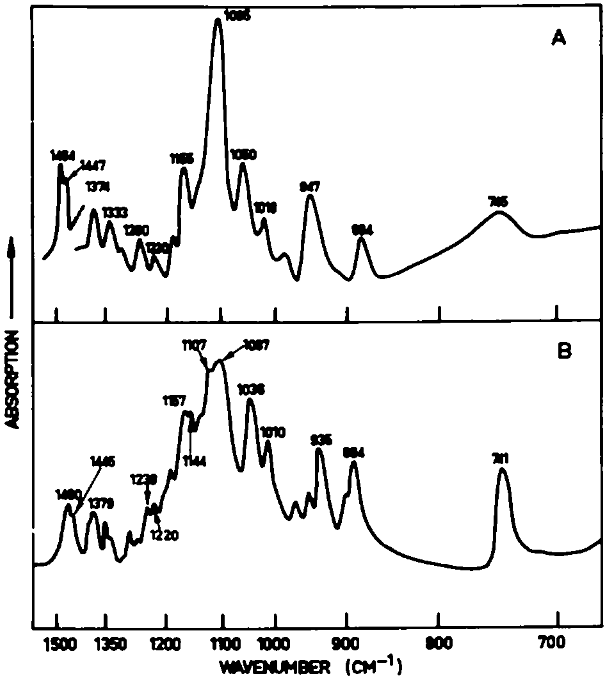

FIG. 3 Spectra of 2,3,4 tri-O-methyl-D-xylopyranose
A. In solution in C_2Cl_4 and CS_2
B. In a KCl disc.

EXPERIMENTAL

The solvents and a number of samples used were the same as described previously.[8] In addition, pure samples of methyl 2,3,4,6- tetra-O-methyl α-D-glucopyranoside and methyl 2,3,4 tri-O-methyl-D-xylopyranoside were kindly supplied by Prof. T. E. Timell, 2-O-methyl-D-glucopyranose and 2,3 di-O-methyl-D-glucopyranose by Dr. E. F. L. Anet and 3-O-methyl-D-xylopyranose and 6-O-methyl-D-glucopyranose by Prof. B. Lindberg. The sample of 3-O-methyl-D-glucopyranose was obtained from Calbiochem. Hexachlorobutadiene was obtained from L. Light & Co., and the KCl was purified by the method of Hales and Kynaston.[24]

NaCl cells of 5 mm pathlength were used for most of the measurements. The spectra were measured on a Grubb Parsons double beam S4 spectrometer equipped with silica and rocksalt prisms. In the C—H stretching region the solvent used was CCl_4 and in the region 1650–1400 cm^{-1} C_2Cl_4. CS_2 was used for the remainder of the spectrum.

In the C—H stretching region hexachlorobutadiene mulls were used as well as KCl discs in obtaining the solid state spectra.

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