Infra-red Spectra of Carbohydrates. Part II. Anomeric Configuration of Some Hexo- and Pento-pyranoses.*

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In Part I, the infra-red spectra (730—960 cm.$^{-1}$) of D-glucopyranose and of its *O*-methyl derivatives were discussed, and systematic differences between the α- and the β-series were observed. In this paper, similar consideration is given to the acetates of D-glucopyranose, and to derivatives of galactopyranose, mannopyranose, xylopyranose, and arabopyranose. The new spectra provide additional evidence for the tentative assignments given in Part I, and are in agreement with the rules governing the assumption by a sugar of its more stable chair form.

IN previous communications (Barker, Bourne, Stacey, and Whiffen, *Chem. and Ind.*, 1953, 196; Part I *) it was shown that the infra-red spectra of D-glucopyranose derivatives display, in the frequency range 730—960 cm.$^{-1}$, three principal sets of bands. Type 1, exhibited by α-anomers at 917 ± 13 cm.$^{-1}$, and by β-anomers at 920 ± 5 cm.$^{-1}$, was attributed tentatively to a ring vibration analogous to that shown by tetrahydropyran at 875 cm.$^{-1}$ (cf. Burket and Badger, *J. Amer. Chem. Soc.*, 1950, **72**, 4397), which includes a considerable contribution from the ring C–O–C antisymmetrical stretching. Type 2, revealed by α-anomers at 844 ± 8 cm.$^{-1}$, and by β-anomers at 891 ± 7 cm.$^{-1}$, was believed to be one of the $C_{(1)}$–H deformation modes. Type 3, shown by α-anomers at 766 ± 10 cm.$^{-1}$,

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* Part I, *J.*, 1954, 171.

and by β-anomers at 774 ± 9 cm.$^{-1}$, was suspected of being the ring breathing frequency exhibited by tetrahydropyran at 813 cm.$^{-1}$ (Burket and Badger, *loc. cit.*).

The present investigation was instigated to determine whether vibrations of types 1, 2, and 3 were exhibited by acetates of D-glucopyranose, and by derivatives of the pyranose forms of other hexoses and of pentoses. It was also an attempt to obtain further evidence for the tentative assignments given to these vibrations in Part I.

EXPERIMENTAL

The spectra were measured with a Grubb–Parsons single-beam spectrometer, with a sodium chloride prism, by the " Nujol " mull technique. The derivatives investigated were crystalline, unless otherwise stated, and wherever possible their authenticity was confirmed by melting point and specific rotation. The Tables show the frequencies (cm.$^{-1}$) of the absorption bands, together with indications of their relative intensities. They list also those carbon atoms in the pyranose rings which carry an equatorial hydrogen atom; the assumptions made in determining these carbon atoms are (i) that a pyranose ring takes up a chair form in preference to any boat form whenever both are structurally possible, and (ii) any axial substituent (other than hydrogen) on the pyranose ring introduces an element of instability into the conformation—especially important are an axial oxygen atom on position 2 when its C–O valency bisects the two C–O valencies of carbon atom 1, and an axial hydroxymethyl group at position 5 on the same side of the ring as an axial hydroxyl, or substituted hydroxyl, group (Reeves, *J. Amer. Chem. Soc.*, 1950, **72**, 1499).

DISCUSSION

Identification of Anomers.—The use of the type 2 absorption peaks in the determination of anomeric configuration (Part I) has been extended to other monosaccharide derivatives of D-glucose, particularly those containing the *O*-acetyl group (Table 1). All those having the α-configuration displayed type 2*a* absorption at 843 ± 4 cm.$^{-1}$. This region was transparent in the spectra of those β-anomers given in Table 1. However, derivatives of β-D-glucose in which a benzene ring was incorporated (*e.g.*, phthalimido- and trityl derivatives) sometimes displayed absorption in this region due to the benzene ring (*e.g.*, methyl 2 : 3 : 4-tri-*O*-acetyl-6-deoxy-6-phthalimido-β-D-glucopyranoside, 836 m; phenyl α-D-glucopyranoside, 836 s; phenyl β-D-glucopyranoside, 827 m).

Type 2*a* absorption is shown also by octa-acetates of disaccharides in the D-glucose series possessing at least one of the sugar moieties in the α-configuration, irrespective of whether this α-unit constitutes the non-reducing (*e.g.*, β-*iso*maltose octa-acetate, 825 cm.$^{-1}$; β-maltose octa-acetate, 834 cm.$^{-1}$) or the reducing (*e.g.*, α-cellobiose octa-acetate, 840 cm.$^{-1}$; α-gentiobiose octa-acetate, 840 cm.$^{-1}$) portion of the disaccharide.

All the acetates of β-D-glucopyranose examined gave an absorption band (type 2*b*), of moderate or strong intensity, at 890 ± 8 cm.$^{-1}$ (Table 1). As stated in Part I, some of the type 1 absorptions of the α-compounds lie in the same range as the type 2*b* absorptions of the β-compounds, and so the presence of a band at *ca.* 890 cm.$^{-1}$ is not conclusive evidence for a β-glucose unit. There is an additional complication when dealing with acetates inasmuch as the ester groups themselves absorb near this frequency region.

An examination of the infra-red spectra of *O*-methyl- and *O*-acetyl-pyranose derivatives of other aldohexoses and of aldopentoses, of their methyl-glycosides, and of the free sugars themselves, revealed the results given in Tables 2, 3, and 4; the mean frequencies and standard deviations for the hexoses are summarised in Table 5.

It will be seen that the pyranose derivatives of mannose and galactose resemble those of glucose in that they display absorption bands of types 2(*a* or *b*) and 3, and probably also of type 1, but the high proportion of acetates in the compounds available made it impossible to distinguish bands of the latter type from other C–O–C vibrations. The type 2*a* absorption, which is so useful for characterising derivatives of α-D-glucose, was shown by all the α-galactose and α-mannose compounds, but unfortunately a few of the β-anomers showed a band in the same region; further work will be necessary before it can be decided whether these apparent anomalies were in fact due to impurities. In the

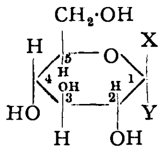


TABLE 1. *Derivatives of* D-*glucopyranose.*

α-D-Glucopyranose : X = H ; Y = OH. Equatorial hydrogen on $C_{(1)}$.
β-D-Glucopyranose : X = OH ; Y = H. No equatorial hydrogen atoms.
The conformation in each case above is C1 (Reeves, *loc. cit.*).
Key : br = broad ; m = moderate strength ; s = strong ; v = very ; w = weak.

Compound	Frequencies (cm.$^{-1}$) of absorption peaks								
	C–O–C vibrations, type 1, etc.					Type 2*b* ?	Other peaks	Type 2*a*	Type 3
α-D-Glucopyranose	—	—	914 s	—	—	—	—	837 s	774 s
1 : 3 : 4 : 6-tetra-*O*-acetyl-2-deoxy-	956 s	927 vs	911 s	902 s	876 w	—	865 vw †	849 m	747 m
2-acetamido-1 : 3 : 4 : 6-tetra-*O*-acetyl-2-deoxy-	942 s	—	914 w	896 w	884 w	—	—	842 w	745 w
1 : 2 : 3 : 4-tetra-*O*-acetyl-6-*O*-methyl-	942 m	926 s	916 s	898 s	891 s	—	—	847 w	741 m
1 : 2 : 3 : 4 : 6-penta-*O*-acetyl-	942 vs	935 vs	911 s	905 s	886 m	—	—	841 s	743 m
2 : 3 : 4 : 6-tetra-*O*-acetyl-1-bromo-1-deoxy-	—	925 vs	910 s	892 m	—	—	—	845 s	751 m
Methyl α-D-glucopyranoside	—	—	—	896 s	—	—	—	840 s	745 s
3 : 4 : 6-tri-*O*-acetyl-2-*O*-methyl-	—	922 vs	—	—	888 s	—	—	842 w	754 s, 743 s
β-D-Glucopyranose	—	—	909 m	—	—	896 vs	856 w *	—	—
1 : 2 : 3 : 4-tetra-*O*-acetyl-	956 m	927 m	909 s	—	882 m	897 m	—	—	781 w
1 : 2 : 3 : 4 : 6-penta-*O*-acetyl-	949 m	938 m	911 m	—	872 w	898 m	—	—	—
Methyl β-D-glucopyranoside	961 s	—	—	—	—	884 s	—	—	783 m
2 : 3 : 4-tri-*O*-acetyl-	966 m	935 vw	907 s	—	—	876 m	—	—	—
2 : 3 : 4-tri-*O*-acetyl-6-bromo-6-deoxy-	957 m	—	903 vs	—	—	885 m	853 w *	—	—
2 : 3 : 4 : 6-tetra-*O*-acetyl-	949 m	—	911 s	903 vs	867 m	894 vs	—	—	—
3-acetamido-2 : 4 : 6-tri-*O*-acetyl-3-deoxy-	—	924 m	908 m	—	—	892 s	828 w	—	731 m

* Possibly due to a trace of the α-anomer. † Probably due to the CH_2-group.

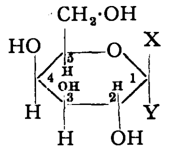


TABLE 2. *Derivatives of* D-*galactopyranose.*

α-D-Galactopyranose : X = H ; Y = OH. Equatorial hydrogens on $C_{(1)}$ and $C_{(4)}$.
β-D-Galactopyranose : X = OH ; Y = H. Equatorial hydrogen on $C_{(4)}$.
The conformation in each case above is C1 (Reeves, *loc. cit.*).

Compound	Frequencies (cm.$^{-1}$) of absorption peaks									
	C–O–C vibrations, type 1, etc.				Type 2*b*	Type 2*c*	Other peaks	Type 2*a*	Other peaks	Type 3
α-D-Galactopyranose	953 vs	—	—	—	—	888 vw	—	833 vs	792 vs	764 vs
1 : 2 : 3 : 4-tetra-*O*-acetyl-6-deoxy-	947 m	926 vs	898 s	—	—	868 w	—	820 m	—	737 s
2 : 3 : 4 : 6-tetra-*O*-acetyl-1-bromo-1-deoxy-	942 s	907 vs	894 s	884 s	—	870 m	857 m	839 m	822 w	757 m, 743 m
Methyl α-D-galactopyranoside	—	923 s	—	—	—	868 s	—	818 vs	—	784 vs
2 : 3 : 4 : 6-tetra-*O*-acetyl-	947 s	936 vs	907 vs	890 s	—	868 w	846 w	833 m	820 w	757 s, 748 s
6-deoxy-2 : 3 : 4-tri-*O*-methyl-	947 vs	—	907 s	—	—	859 m	—	810 vs	—	736 vs
β-D-Galactopyranose	943 m	—	—	—	897 s	881 s	—	—	831 mbr *	776 vs
1 : 2 : 3 : 4 : 6-penta-*O*-acetyl-	956 s	928 m	914 m	—	896 vs	865 s	—	—	—	725 m
6-deoxy-	961 s	—	—	—	914 m	876 m	—	—	814 vs	768 m
Methyl β-D-galactopyranoside	—	940 m	—	—	887 m	868 s	—	—	821 vw	782 s
2 : 3 : 4-tri-*O*-methyl-	—	933 m	—	—	888 m	870 m	—	—	—	757 vs
6-deoxy-2 : 3 : 4-tri-*O*-methyl-	958 s	935 m	—	—	886 s	872 s	—	—	—	727 s
2 : 3 : 4 : 6-tetra-*O*-methyl-	—	933 m	—	—	898 s	872 m	—	—	—	751 vs
2 : 3 : 4 : 6-tetra-*O*-acetyl-	952 vs	—	905 vs	—	896 s	879 w, 868 s	—	—	—	727 s

* Possibly due to the α-anomer.

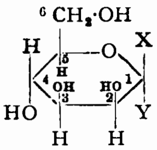


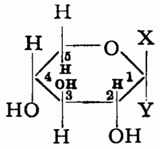
TABLE 3. *Derivatives of mannopyranose.*

α-D-Mannopyranose : X = H ; Y = OH. Equatorial hydrogens on $C_{(1)}$ and $C_{(2)}$.
β-D-Mannopyranose : X = OH ; Y = H. Equatorial hydrogen on $C_{(2)}$.
The conformation in each case above is C1 (Reeves, *loc. cit.*).

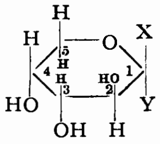
Compound	Frequencies (cm.$^{-1}$) of absorption peaks									
	C-O-C vibrations, type 1, etc.				Type 2*b*	Type 2*c*	Other peaks	Type 2*a*	Type 3	Other peaks
α-D-Mannopyranose										
3 : 4-di-*O*-methyl-, monohydrate ...	966 m	937 w	913 w	—	—	878 m	—	841 s	794 vs	746 s
3 : 4 : 6-tri-*O*-methyl-	966 vs	947 vs	—	894 s	—	871 s	—	818 s	791 vs	—
α-L-Mannopyranose										
6-deoxy-, monohydrate	973 vs	—	907 s	—	—	872 s	—	824 s	798 vs	—
Methyl α-D-mannopyranoside	972 s	—	914 w	—	—	888 w	—	843 m	808 s	—
2 : 3 : 4-tri-*O*-acetyl-	965 vs	928 vs	916 vs	—	—	886 vs	—	837 w	818 m, 789 s	756 vs
2 : 3 : 4 : 6-tetra-*O*-acetyl-	—	935 s	911 m	900 m	—	886 w	—	830 w	792 m	—
2 : 3 : 4 : 6-tetra-*O*-methyl-	966 vs	951 vs	925 m	901 w	—	876 s	—	840 s	792 s	—
Methyl α-L-mannopyranoside										
6-deoxy-	961 vs	—	905 s	—	—	874 s	—	833 s	799 s	—
2 : 3 : 4-tri-*O*-acetyl-6-deoxy-	974 vs	949 vs, 935 vs	905 vs	898 vs	—	881 vs	—	834 s	795 s, 788 s	—
β-D-Mannopyranose	—	938 m	—	—	896 m	861 m	854 m	—	770 s	—
1 : 2 : 3 : 4 : 6-penta-*O*-acetyl-	971 s	947 vs, 933 vs	905 s	—	888 s	880 s	850 w	—	756 s	—
Mannan (1 : 4-β-polysaccharide)	—	938 s	—	—	888 m	867 s	—	—	812 s, 803 vs	—
Methyl β-D-mannopyranoside *	—	947 m	928 m	—	896 m	875 m	830 m	—	795 s	—
2 : 3 : 4 : 6-tetra-*O*-acetyl-	956 vs	947 vs	—	—	898 vs	863 s	—	—	747 s	—

* Syrup.

TABLE 4. *Derivatives of xylopyranose and arabopyranose.*



α-D-Xylopyranose : X = H ; Y = OH. Equatorial hydrogen on $C_{(1)}$.
β-D-Xylopyranose : X = OH ; Y = H. No equatorial hydrogen atoms.
The conformation in each case above is C1 (Reeves, *loc. cit.*).



α-D-Arabopyranose : X = H ; Y = OH. Equatorial hydrogen on $C_{(4)}$.
β-D-Arabopyranose : X = OH ; Y = H. Equatorial hydrogens on $C_{(1)}$ and $C_{(4)}$.
The conformation in each case above is 1C (Reeves, *loc. cit.*).

Compound	Frequencies (cm.$^{-1}$) of absorption peaks		
		830—855 cm.$^{-1}$	Type 3
α-D-Xylopyranose	933 s, 903 s	—	760 s
2 : 3 : 4-tri-*O*-methyl-	935 vs, 903 vs, 892 vs	—	742 s
2 : 3 : 4-tri-*O*-acetyl-	929 s, 914 s, 898 m, 889 m, 878 s	—	759 s
2 : 3 : 4-tri-*O*-acetyl-1-bromo-1-deoxy-	934 vs, 901 vs, 882 s, 873 vs	—	753 m, 740 s
Methyl α-D-xylopyranoside	938 s, 896 s	—	740 s
β-L-Xylopyranose			
1 : 2 : 3 : 4-tetra-*O*-acetyl-	940 m, 909 s, 895 s, 878 s	—	—
Xylan (β-1 : 4-D-polysacc.)	895 m	—	—
2 : 3-di-*O*-acetyl-	930 w, 894 s, 876 s	—	—
Methyl β-D-xylopyranoside	935 m, 920 m, 896 s	—	—
2 : 3 : 4-tri-*O*-methyl-	937 m, 886 s	—	—
α-D-Arabopyranose			
1 : 2 : 3 : 4-tetra-*O*-acetyl-	947 m, 914 m, 898 m, 879 w, 861 w	—	749 s
Methyl α-D-arabopyranoside	938 vs, 914 s, 878 s	—	776 s, 772 s
β-D-Arabopyranose	941 m, 890 s	840 s	781 vs
2 : 3 : 4-tri-*O*-acetyl-1-bromo-1-deoxy- (L-isomer)	938 s, 930 s, 890 s, 870 m	853 s	759 s
Methyl β-D-arabopyranoside	944 m, 923 m, 882 s	843 m, 836 m	775 s
2 : 3 : 4-tri-*O*-methyl-	933 vs, 905 s	854 s	744 vs

arabinose series, the presence or absence of absorption at 830—855 cm.$^{-1}$ again seems to afford a good method of differentiating between α- and β-forms; it is interesting that in this case it is the β-compounds which show the absorption in the region of the 2*a* band of hexoses, but we prefer at this stage not to assign the vibration. The xylopyranose series is exceptional inasmuch as neither the α- nor the β-anomers show absorption at 830—855 cm.$^{-1}$; however, the presence or absence of type 3 absorption (749 ± 10 cm.$^{-1}$) can apparently be used here for the differentiation of anomers.

TABLE 5.

Pyranose sugar derivatives of:	Absorption (cm.$^{-1}$) of:			
	Type 2*a*	Type 2*b*	Type 2*c*	Type 3
α-D-Glucose	843 ± 4	—	—	753 ± 17
β-D-Glucose	—	890 ± 8		
α-D-Galactose	825 ± 11	—	871 ± 7	752 ± 20
β-D-Galactose	—	895 ± 9		
α-D-Mannose	833 ± 8	—	876 ± 9	791 ± 18
β-D-Mannose	—	893 ± 6		

It is to be expected that optical enantiomorphs will show identical infra-red spectra (provided that they have been isolated in the same crystalline form), and this was found to be the case, over the frequency range 1790—630 cm.$^{-1}$, for the D- and L-forms of β-arabopyranose, methyl α-arabopyranoside, β-xylopyranose tetra-acetate, and α-xylopyranose. It follows, therefore, that the conclusions reached above are equally valid for the D- and the L-series.

Type 2*c* absorption, displayed by derivatives of D-galactopyranose and D-mannopyranose (irrespective of their anomeric configuration) but not by derivatives of D-glucose, seems to offer a useful method for distinguishing between derivatives of these three hexoses which are identically substituted. In addition it may prove valuable in the polysaccharide field for distinguishing a polyglucosan from a polymannan or a polygalactan. It is shown also by the galactose-containing disaccharides; for example, melibiose and lactose each has a peak at 872 cm.$^{-1}$, which is absent from the spectra of *iso*maltose and cellobiose.

Caution must be exercised in any interpretation of the infra-red spectra of syrups since a marked peak movement was observed in passing from crystalline to syrupy glucose. A syrupy α,β-mixture of D-glucose showed both type 2*a* and 2*b* absorption peaks, but these were somewhat displaced from their usual positions. Thus absorption of type 2*a*, present in crystalline α-D-glucose at 837 cm.$^{-1}$, now appeared at 849 cm.$^{-1}$.

Evidence for Assignment.—It was suggested in Part I that the vibrations associated with type 2*a* and 2*b* absorptions were C–H deformations in which the hydrogen on $C_{(1)}$ was involved intimately. It was believed that the difference between the α- and the β-glucose frequencies was related to the fact that this hydrogen atom in the α-anomer lies in the equatorial belt of the chair form of the six-membered ring and in the β-anomer in the axial position. It may be that, as in tetrahydropyran (Burket and Badger, *loc. cit.*), the axial hydrogen atoms on $C_{(1)}$ and $C_{(5)}$ of a pyranose sugar ring are closer together than in *cyclo*hexane, and those on $C_{(2)}$ and $C_{(4)}$ are further apart. Since the most stable conformation of a D-glucopyranose ring involves an axial hydrogen atom on $C_{(5)}$, it is possible that during deformation the axial hydrogen atoms on $C_{(1)}$ and $C_{(5)}$ come into van der Waals contact, or very nearly so, and that this leads to an increased frequency.

Additional evidence for the assignment of type 2*a* absorption to an equatorial $C_{(1)}$–H deformation is that, besides derivatives of α-D-glucopyranose, those of α-D-galactopyranose and α-D-mannopyranose also display type 2*a* absorption (Table 5), and this absorption is independent of *O*-substituents. All of these sugars, in the most stable conformation of their pyranose rings, are known to have an equatorial hydrogen atom on $C_{(1)}$. It remains to be seen whether pentoses in general exhibit type 2*a* absorption; if they do, then the absorption at 830—855 cm.$^{-1}$ in derivatives of β-D-arabinose is consistent with this generalisation, and the only exceptions, as yet, are the derivatives of α-D-xylopyranose which have a $C_{(1)}$–H in the equatorial position and yet fail to display absorption in this range. The reason for this may be that the lack of a hydroxymethyl group on $C_{(5)}$ and the absence of any axial hydroxyl group round the ring (other than on $C_{(1)}$) markedly reduce the change of dipole moment during the equatorial $C_{(1)}$–H deformation.

Type 2*b* absorption is shown by derivatives of β-D-glucopyranose, β-D-galactopyranose, and β-D-mannopyranose, all of which have an axial $C_{(1)}$–H in their most stable conformation. If this generalisation is applicable to pentoses, then suitable candidates can be found in the spectra of pyranose derivatives of α-D-arabinose and β-D-xylose.

In a strict comparison of the corresponding derivatives of D-galactopyranose and D-mannopyranose with those of D-glucopyranose, the derivatives of the two former hexoses almost invariably displayed an extra absorption peak (type 2*c*) at *ca.* 875 cm.$^{-1}$ (Table 5), which appeared to be independent of *O*-substituents, and of anomeric character. It is believed that this absorption is due to deformations of the equatorial C–H bonds at positions 4 and 2 in galactopyranose and mannopyranose, respectively. Such a rise of frequency from *ca.* 840 cm.$^{-1}$ for a $C_{(1)}$–H equatorial deformation to *ca.* 875 cm.$^{-1}$ for a $C_{(2)}$–H or $C_{(4)}$–H equatorial deformation is consistent with subjection of the equatorial hydrogen atoms on $C_{(2)}$ and $C_{(4)}$ to van der Waals forces from neighbouring groups which are stronger than those affecting the equatorial hydrogen on $C_{(1)}$.

Finally, to the question of the value of the deformation frequency of an axial C–H group, other than $C_{(1)}$–H, no answer can be given because the region above 890 cm.$^{-1}$, where such an absorption might occur, also contains absorption peaks due to type 1 vibrations and to the in-phase C–O stretching mode of methyl ethers and of acetates.

As mentioned in Part I, the type 3 peak intensity is very sensitive to changes in sugar configuration; thus decreased intensity was observed in derivatives of β-D-glucopyranose, which possesses no axial C–O bonds. This decrease is even more marked in derivatives of β-D-xylopyranose, which differs from β-D-glucopyranose only in the absence of a hydroxymethyl group on $C_{(5)}$, no absorption of type 3 being observed in any derivative so far studied. The symmetrical character of the vibration is emphasised also by *scyllo*inositol, a centrosymmetrical cyclitol, in which all the C–O bonds are equatorial, and which does not display type 3 absorption in the infra-red, in agreement with the selection rules. The lower frequencies of the type 3 absorption in sugars, and more particularly of their fully substituted acetates, compared with that observed in tetrahydropyran (813 cm.$^{-1}$), is to be expected from the extra weight involved.

Since the publication of our first paper on this topic, Whistler and House (*Analyt. Chem.*, 1953, **25**, 1463) have reported independently that infra-red spectra can be used to distinguish between anomeric forms of carbohydrates; many of the characteristic bands were however in a higher frequency range than those reported herein.

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