

Infra-red Spectra of Carbohydrates. Part IV. Characterisation of Furanose Derivatives.*

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Compounds containing a furanose or hydrofuranol ring are shown to exhibit infra-red absorption of types A, B, C, and D at 924 ± 13 , 879 ± 7 , 858 ± 7 , and 799 ± 17 cm^{-1} , respectively. Similar absorption is exhibited by derivatives containing two such fused rings or a hydrofuranol ring fused to a pyranose ring (3 : 6-anhydro-derivatives). Tentative assignments are made.

PREVIOUS work on the infra-red spectra of saturated five-membered ring systems has been concerned mainly with the assignment, to various modes of ring and methylene vibrations, of the absorption peaks of cyclopentane (Aston, Schumann, Fink, and Doty, *J. Amer. Chem. Soc.*, 1941, **63**, 2029; Miller and Inskip, *J. Chem. Phys.*, 1950, **18**, 1519; Kilpatrick, Pitzer, and Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2483; Tschamler and Voetter, *Monatsh.*, 1952, **83**, 303, 1228) and of tetrahydrofuran (Tschamler and Voetter, *loc. cit.*). The precise conformation of such systems, vital for any rigid assignment, has been much discussed.

* Part III, *J.*, 1954, 4211.

In a regular pentagon the interior angles are very close to the tetrahedral value (108° ; cf. $109^\circ 28'$) so the planar structure is stabilised by forces tending to maintain tetrahedral bond angles. Conversely, the repulsions between the hydrogen atoms of neighbouring methylene groups, at a maximum in the planar structure, tend to produce torsional forces around the C-C bonds which would pucker the ring (Miller and Inskeep, *loc. cit.*). It is now generally agreed that neither *cyclopentane* nor tetrahydrofuran has a completely planar ring, but that the puckering is so small (Kilpatrick, Pitzer, and Spitzer, *loc. cit.*, calculate for *cyclopentane* a maximum out-of-plane displacement of 0.2 \AA) that, with a few exceptions, the selection rules for a planar ring can be followed. On this basis Tschamler and Voetter (*loc. cit.*) made the assignments of ring frequencies given in Table 1.

TABLE 1. Assignments of ring frequencies.

Type of ring vibration	Frequencies (cm. ⁻¹)	
	<i>cyclo</i> Pentane	Tetrahydrofuran
Out-of-plane	207; 283	215; 276
Bending	546?	596
Symmetrical ring breathing	886	913
Stretching	1030; 1207	1028, 1071; 1174

The present work, which is confined to the frequency range $710\text{--}1000 \text{ cm.}^{-1}$, is concerned with compounds which can be regarded as derivatives of tetrahydrofuran, such as the furanose forms of sugars and certain anhydro-derivatives of polyhydric alcohols; it illustrates how a series of infra-red absorption peaks may be useful in the identification of such a ring system, whether free, or fused either to a similar ring or to a pyranose ring.

EXPERIMENTAL

The spectra were measured with a Grubb-Parsons single-beam spectrometer, with a sodium chloride prism, the "Nujol" mull technique being used. The Tables show the frequencies (cm.⁻¹) of the absorption bands, together with indications of their relative intensities.

DISCUSSION

Identification of a Furanose or Hydrofuranol Ring.—All those compounds examined (excluding tetrahydrofuran itself) having a single furanose or hydrofuranol ring showed type A absorption at $924 \pm 13 \text{ cm.}^{-1}$ and type D absorption at $799 \pm 17 \text{ cm.}^{-1}$ (Table 2). In addition most of these compounds also showed type B absorption at $879 \pm 7 \text{ cm.}^{-1}$ and type C at $858 \pm 7 \text{ cm.}^{-1}$.

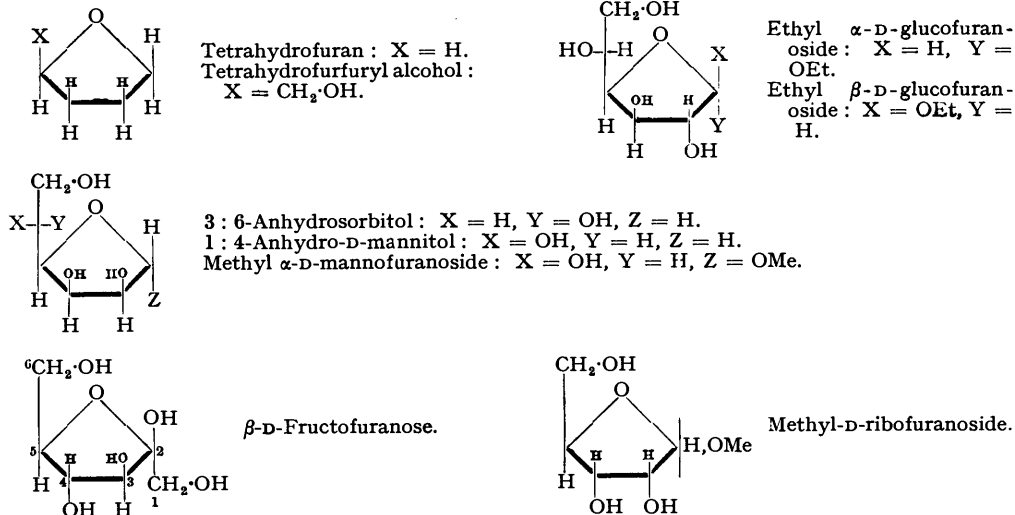
When two such five-membered rings were fused together (Table 3) absorption attributable to type A and type D generally appeared in the form of doublets, still, however, with their respective average frequencies at 917 ± 15 and $798 \pm 16 \text{ cm.}^{-1}$. In the case of 1 : 4-3 : 6-dianhydro-D-mannitol, where two identical hydrofuranol rings are fused together, single absorption peaks only were observed at 923 and 816 cm.^{-1} , respectively. In addition most of these compounds (Table 3) also showed absorption of type B at $880 \pm 5 \text{ cm.}^{-1}$ and of type C at $848 \pm 13 \text{ cm.}^{-1}$.

Where a hydrofuranol ring is fused to a pyranose ring (Table 4) absorption peaks attributable wholly or in part to vibrations associated with types A (not distinguished from types 1 or 2*b*), B ($870 \pm 7 \text{ cm.}^{-1}$), C ($838 \pm 16 \text{ cm.}^{-1}$), and D ($798 \pm 21 \text{ cm.}^{-1}$) can still be found.

Assignment.—(i) *Type A.* This absorption can be assigned to the symmetrical ring-breathing frequency. The fact that, in this range, the strongest polarised Raman shifts appear at 886 cm.^{-1} in the spectrum of *cyclopentane* and at 913 cm.^{-1} in that of tetrahydrofuran is strong evidence in support of such an assignment (Tschamler and Voetter, *loc. cit.*). With two dissimilar hydrofuranol rings fused together, the "doubling" observed in type A absorption is to be expected because of interactions between the rings.

When a hydrofuranol ring is fused to a pyranose ring as in the case of 3 : 6-anhydro-sugar derivatives (Table 4), the five-membered ring will tend to exist as nearly planar as possible, the pyranose ring adopting either the 1C chair form or the 1B boat form, depending on which form has the smallest total of non-bonded interactions between its polar groups

TABLE 2. Furan derivatives.



Key: m = moderate strength; s = strong; v = very; w = weak.

Compound	Frequencies (cm. ⁻¹) of absorption peaks							Other peaks
	Other peaks	Type A	Other peaks	Type B	Type C	Type 2a	Type D	
Tetrahydrofuran †	—	913 s	—	—	—	—	—	—
Tetrahydrofurfuryl alcohol	980 s	920 s	896 w	870 m	850 m	—	810 s	—
Ethyl α -D-glucofuranoside	951 m *	927 w	915 s, 902 w	884 w	853 s	—	806 s, 778 vs	769 vs †
Ethyl β -D-glucofuranoside	966 w, 940 s *	928 s	—	886 s	855 m	—	794 s	767 m †
3:6-Anhydrosorbitol	981 s	933 s	—	886 s	867 s	—	781 m	—
1:4-Anhydro-D-mannitol	995 vs, 949 vs	929 s	—	880 s	868 s, 860 s	—	782 s	—
Methyl α -D-mannofuranoside	986 vs, 958 vs *	904 m	—	884 vs	868 m	—	783 vs	—
2:3:5:6-tetra-O-acetyl-	986 s, 971 s,* 958 s,* 942 s *	898 s	—	—	(864 w)	—	819 m, 778 m	758 m
Methyl D-fructofuranoside, 3:4:6-tri-O-methyl-§	967 vs *	943 vs	—	888 w	847 w	—	833 s	—
Inulin (poly-1:2- β -D-fructofuranoside)	984 vs	933 vs	—	872 m	—	—	813 m	—
O- α -D-Glucopyranosyl-(1 \rightarrow 2)-O- β -fructofuranosyl-(1 \rightarrow 2) β -D-fructofuranoside	—	928 vs	—	872 m	854 m	832 m	812 m	—
Levan (poly-2:6- β -D-fructofuranoside)	984 w, 971 m	919 vs	—	874 m	—	—	803 m	—
O- α -D-Glucopyranosyl-(1 \rightarrow 2)-O- β -D-fructofuranosyl-(6 \rightarrow 2) β -D-fructofuranoside	990 vs, 947 s	924 vs	—	873 m	855 w	842 m, 831 w	806 s	729 m
Methyl D-ribofuranoside §	972 m	942 m	—	—	—	—	782 m	—
Mean and standard deviation	—	924 \pm 13	—	879 \pm 7	858 \pm 7	—	799 \pm 17	—

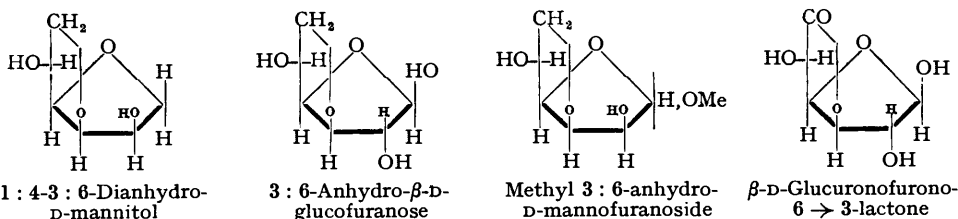
* C-O stretching mode of methyl and ethyl ethers and acetates.

† CH₂ rocking of ethyl group.

‡ Cf. Shreve, Heether, Knight, and Swern, *Anal. Chem.*, 1951, **23**, 277.

§ Syrup.

TABLE 3. Derivatives containing two fused hydrofuranol rings.



Compound	Frequencies (cm. ⁻¹) of absorption peaks					Other peaks
	Other peaks	Type A	Type B	Type C	Type D	
1 : 4-3 : 6-Dianhydro-D-mannitol	966 s	923 s	—	842 m	816 vs	—
2 : 5-di-O-methyl-	981 vs, 944 s *	915 s	880 vs	846 s	814 m, 802 m	789 m, 753 m
1 : 4-3 : 6-Dianhydro-sorbitol †	976 s, 951 m	922 m	884 m	865 m	830 s, 733 s	—
3 : 6-Anhydro-D-glucofuranose	964 vs	935 m, 906 m	875 m	867 m	798 m, 783 s	711 m
2-deoxy-	975 vs, 941 m	928 m, 896 w	887 w	833 m	798 m, 783 s	—
D-Glucuronofurono-(?)6 \rightarrow 3-lactone	945 s	933 vs, 903 s	—	840 s	802 s, 793 s	765 s
Methyl 3 : 6-anhydromannofuranoside	970 vs, 953 vs *	933 m, 895 vs	876 vs	846 m	806 s, 781 vs	711 m
Mean and standard deviation	—	917 \pm 15	880 \pm 5	848 \pm 13	798 \pm 16	—

* C-O stretching mode of methyl ethers.

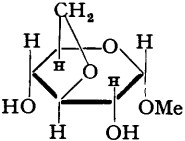
† Syrup.

(Foster, Overend, and Vaughan, *J.*, 1954, 3625). Under such conditions, the main absorption peaks to be expected in this region are those analogous to types A, B, C, and D of a single hydrofuranol ring and those of types 1, 2*a*, 2*b*, 2*c*, and 3 of a single pyranose ring. It will be recalled (Barker, Bourne, Stacey and Whiffen, *J.*, 1954, 171; Barker, Bourne, Stephens, and Whiffen, *J.*, 1954, 3468) that type 1 at *ca.* 910 cm.⁻¹ and type 3 at *ca.* 760 cm.⁻¹ have been assigned to vibrations of the pyranose ring, while types 2*a* at *ca.* 830 cm.⁻¹, 2*b* at *ca.* 890 cm.⁻¹, and 2*c* at 870 cm.⁻¹ were believed to involve the deformation modes of an equatorial C₍₁₎-H, of an axial C₍₁₎-H, and of other equatorial carbon-hydrogen bonds around the pyranose ring (*e.g.*, C₍₂₎-H and C₍₃₎-H), respectively. Table 5 shows the various equatorial and axial dispositions of the carbon hydrogen bonds around the pyranose ring of a 3 : 6-anhydro-sugar derivative adopting a given conformation. No attempt has been made in the case of the 3 : 6-anhydro-sugar derivatives to distinguish absorption attributable to type A of the hydrofuranol ring from that of type 1 or 2*b* of the pyranose ring since they appear within the same range.

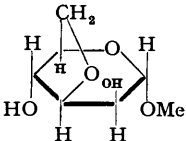
(ii) *Type D*. This absorption can be assigned tentatively to a carbon-hydrogen deformation mode where the hydrogen is present on a carbon atom directly attached to a ring-oxygen atom of a furanose or hydrofuranol ring. Whereas in the pyranose ring the carbon-hydrogen bond can be either axial or equatorial, such bonds are in relatively equivalent positions where the carbon atom is incorporated in a furanose ring and a general differentiation between α - and β -furanose glycosides is not to be expected on such a basis. Table 2 shows that a carbon-hydrogen bond incorporated in the grouping (I) displays an absorption frequency (type D) relatively independent of X (other than X = H). Further evidence for such an assignment is that while methylcyclopentane does not show type D absorption, methyltetrahydrofuran (Barrow and Searles, *J. Amer. Chem. Soc.*, 1953, 75, 1175) and tetrahydrofurfuryl alcohol do so at 800 and 810 cm.⁻¹, respectively. It is interesting that in the 3 : 6-anhydro-aldopyranose derivatives (Table 5), the pyranose ring does not apparently interfere with type D absorption and still retains its symmetrical type 3 ring-breathing frequency at 747 \pm 11 cm.⁻¹.

(iii) *Types B and C*. It may be that absorptions of types B and C in general arise from

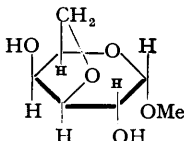
TABLE 4. Derivatives containing fused hydrofuranol and pyranose rings.



Methyl 3 : 6-anhydro- α -D-glucopyranoside



Methyl 3 : 6-anhydro- α -D-mannopyranoside



Methyl 3 : 6-anhydro- α -D-galactopyranoside

Frequencies (cm.⁻¹) of absorption peaks

Compound and probable pyranose conformation	Includes C-O stretching of methyl ethers	Types A, 1, and 2b, Type B (or 2c), Other peaks, Type C (or 2a), Type 2a, Type D, Type 3						
		Types A, 1, and 2b	Type B (or 2c)	Other peaks	Type C (or 2a)	Type 2a	Type D	Type 3
Methyl α -D-glucopyranoside (C1)	992 vs	896 s	—	—	—	840 s	—	745 s
3 : 6-anhydro- (1C)	987 vs, 942 s	909 vs, 892 vs	868 s	—	842 s	—	815 vs	742 vs
2-deoxy- (C1)	966 s, 914 s	896 s	—	870 s *	—	837 vs	—	760 s
3 : 6-anhydro-2-deoxy- (1C)	997 s, 978 s	916 vs, 909 vs	868 vs	—	843 vs	—	826 s, 818 s, 790 vs	737 s
Methyl α -D-mannopyranoside (C1)	972 s	914 m	888 w	—	—	843 m	—	808 s
3 : 6-anhydro- (1C)	990 s, 967 m, 942 s	919 m, 913 s	878 s	—	849 m	—	801 s	757 s
3 : 6-anhydro-2-O-methyl- (1C)	987 vs, 973 vs, 963 vs	929 vs, 907 s	873 vs	—	853 s	—	823 vs, 810 vs	767 s, 754 s
3 : 6-anhydro-2 : 4-di-O-methyl (1C)	984 m, 965 m	935 s, 901 m	878 m	—	854 w	—	811 m	752 m
Methyl β -D-mannopyranoside † (C1)	947 m	928 m, 896 m	875 s	830 m	—	—	—	795 vs
3 : 6-anhydro- (1C or 1B)	997 vs, 984 vs, 963 vs, 956 vs	897 m	870 s	814 vs	[814 vs]	—	778 vs	739 m
3 : 6-anhydro-2 : 4-di-O-methyl- (1C or 1B)	997 vs, 955 vs	901 m, 892 m	876 m	826 s	850 m	—	775 s	753 m
Methyl α -D-galactopyranoside (C1)	966 s	923 s	868 s	—	—	818 vs	—	784 vs
3 : 6-anhydro- (1C)	987 m, 966 vs	924 vs, 903 vs	865 w	847 s	835 m	—	768 s	734 vs
3 : 6-anhydro-2-deoxy- (1C)	951 vs	914 vs	860 vs	850 vs *	834 vs	—	797 vs	754 s
Methyl β -D-galactopyranoside (C1)	981 s	940 s, 887 s	868 s	821 vw	—	—	—	782 vs
3 : 6-anhydro-2 : 4-di-O-methyl- (1B)	970 vs, 944 vs, 928 vs	907 vs, 898 vs	861 s	811 s	[811 s]	—	767 s	733 s
Mean and standard deviation of 3 : 6-anhydro-derivatives	—	—	870 \pm 7	—	838 \pm 16	—	798 \pm 21	747 \pm 11

* CH₂ rocking (deoxy-group). † Syrup.

TABLE 5. Disposition of carbon-hydrogen bonds in a 3 : 6-anhydro-pyranose derivative.

3 : 6-Anhydro-derivative of :	Conformation of pyranose ring	Equatorial hydrogens on carbon atoms :	Axial hydrogens on carbon atoms :	Expected type 2 absorption
α -D-Glucopyranose	1C	2, 3, 4, 5	1	2b, 2c
α -D-Mannopyranose	1C	3, 4, 5	1, 2	2b, 2c
β -D-Mannopyranose	1C	1, 3, 4, 5	2	2a, 2c
β -D-Mannopyranose	1B	2, 3, 4, 5	1	2b, 2c
α -D-Galactopyranose	1C	2, 3, 5	1, 4	2b, 2c
β -D-Galactopyranose	1B	1, 3, 5	2, 4	2a, 2c

modes of vibration involving the skeletal stretching of the substituents, the latter type being possibly more concerned with the OH group and the former with side chains of the type C·CH(OH)·CH₂·OH (cf. Kohlrausch, Reitz, and Stockmair, *Z. physikal. Chem.*, 1936, B, 32, 229; Barrow, *J. Chem. Phys.*, 1952, 20, 1739). Finally, since it is unlikely that in fused systems one ring can be regarded as the side chain of the other, it is probable that

type B absorption in such systems is due to the rocking vibration of the methylene group in the hydrofuranol ring, although in the case of some 3 : 6-anhydro-derivatives (Table 5) type 2c absorption is to be expected in this same region.

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