Infra-red Spectra of Carbohydrates. Part III. Characterisation of Deoxy-compounds.*

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A single ring-methylene group in (*a*) a quercitol, and (*b*) a 2- or 3-deoxy-derivative of D-glucopyranose, D-mannopyranose, or D-galactopyranose, gives absorption attributable to a CH_2 rocking mode at 853 ± 6 and *ca.* 867 cm.$^{-1}$, respectively. This should assist in the identification of a deoxy-sugar and in distinguishing between a quercitol and an inositol. Absorption characteristic of a *C*-methyl group in derivatives of *cyclo*hexane (including cyclitols) appears at 967 ± 6 cm.$^{-1}$. Additional evidence is obtained for the assignment of the type 2*c* peak to an equatorial hydrogen atom.

As part of a general study of infra-red spectra of carbohydrates (Barker, Bourne, Stacey, and Whiffen, *Chem. and Ind.*, 1953, 196; *J.*, 1954, 171; Barker, Bourne, Stephens, and Whiffen, Part II; * Barker, Bourne, and Carrington, *J.*, 1954, 2125), attempts are being made to determine the characteristic frequencies of certain groups commonly encountered in carbohydrate structures. Although it is not strictly correct to attribute a given frequency solely to a vibration of one particular group in a compound, such an assignment is valuable as a first approximation and may well be useful in subsequent determinations of structures of compounds of the same type. The present communication records the results of a study of the characteristic frequencies of ring-methylene and *C*-methyl groups occurring in deoxy-sugars and in certain cyclitols.

In an analysis of the infra-red spectra of *cyclo*hexane and tetrahydropyran, Burket and Badger (*J. Amer. Chem. Soc.*, 1950, **72**, 4397) assigned vibrations involving the deformation modes of methylene groups to the four following frequency ranges: scissors (or deformation), 1360—1470 cm.$^{-1}$; twisting, 1280—1380 cm.$^{-1}$; wagging, 1170—1300 cm.$^{-1}$; and rocking, 750—1160 cm.$^{-1}$. Our spectra were determined on mulls in liquid paraffin, over the range 730—1000 cm.$^{-1}$ (as in the earlier work), and so presumably only the rocking mode of the methylene group was likely to be observed.

Sheppard and Simpson (*Quart. Reviews*, 1953, **7**, 19) have pointed out that an isolated methyl group attached to a heavy framework, such as a paraffin chain, has three internal deformation vibrations, two doubly degenerate vibrations appearing in the frequency range 1440—1470 cm.$^{-1}$, the third being a symmetrical deformation mode near 1380 cm.$^{-1}$. Each methyl group has also three external vibrations, *viz.*, two rocking modes displayed in the range 800—1250 cm.$^{-1}$, and a torsional motion of the group about the CH_3—C linkage, whose frequency is below 300 cm.$^{-1}$. Thus, for the *C*-methyl group, as for the methylene group, our attention was confined to the rocking modes.

Experimental.—The method for determination of the spectra and the precautions taken to check the purity of each compound examined were as given in Part II. The Tables show the frequencies (cm.$^{-1}$) of the absorption bands, together with indications of their relative intensities.

DISCUSSION

Because of the complexity of the spectra in the frequency range under consideration, it was virtually impossible solely on the basis of the aforementioned work to identify any particular absorption peak with the methylene or *C*-methyl group. Consequently an alternative procedure was adopted: the spectrum of each compound containing one of these groups was compared with the spectra of structurally related compounds devoid of the group, and any additional peaks were noted. Comparison of the extra peaks over the whole series of deoxy-compounds then enabled assignments to be made.

Ring-methylene Groups.—(a) *In cyclitols.* Table 1 records the spectra of three penta-hydroxy*cyclo*hexanes (for the generic name " quercitols " see Angyal and Macdonald,

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* Part II, *J.*, 1954, 3468.

TABLE 1. *Comparison of penta- and hexa-hydroxy*cyclo*hexanes.*

[br = broad; m = moderate strength; s = strong; v = very; w = weak. Means are followed immediately by their standard deviations.]

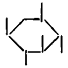
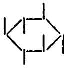
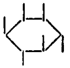
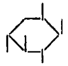
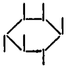
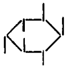
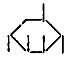
Compound and structure		No. of equatorial H atoms other than CH_2	Frequencies (cm.$^{-1}$) of absorption peaks								
			Other peaks					Type 1 ?	Type 2*c* ?	CH_2 rocking	Type 3 ?
*scyllo*Quercitol		0	992 vs	—	—	934 s	—	—	—	859 s	794 m
*scyllo*Inositol		0	981 vs	—	—	—	—	—	—	—	—
*meso*Inositol		1	997 vs	—	—	928 m	—	896 s	890 s	—	732 s
(−)-*vibo*Quercitol		1	992 vs	—	—	941 vs	—	—	876 s	855 vs	—
*meso*Inositol		1	997 vs	—	—	928 m	—	896 s	890 s	—	732 s
(−)-Inositol		2	997 s	—	—	933 vw	—	898 s	861 s	—	777 s; 763 s
*proto*Quercitol		2	984 s	—	—	941 vw	—	896 vs	871 m	844 s	772 s
*muco*Inositol		3	—	—	—	949 m	—	884 m	870 m	—	800 vs
(+)-Inositol		2	997 s	—	—	933 vw	—	898 s	861 s	—	777 s; 763 s
*scyllo*Quercitol penta-acetate		0	983 s	—	956 s	935 s	913 s	891 w	—	857 s	—
*scyllo*Inositol hexa-acetate		0	983 vs	977 vs	951 vw	930 s	911 m	—	—	—	—
(−)-*vibo*Quercitol penta-acetate		1	—	977 s	953 vs	934 s	909 s	904 s	888 m; 863 w	852 w	727 vs
Mean										853 ± 6	

TABLE 2. *Frequencies of* C-*methyl groups in cyclitols.*

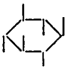
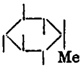
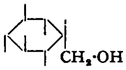
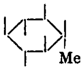
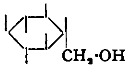
Compound and structure		No. of equatorial H atoms	Frequencies (cm.$^{-1}$) of absorption peaks						
			Other peaks	CH_3 rocking	Other peaks	Type 1 ?	Type 2*c* ?	Other peaks	Type 3 ?
*scyllo*Inositol		0	981 vs	—	—	—	—	—	—
Mytilitol		0	995 vs	963 s	947 m	—	—	—	804 s
Hydroxymytilitol		0	997 vs	—	926 w	—	—	—	806 s
*meso*Inositol		1	997 vs	—	928 m	896 s	890 s	—	732 s
*iso*Mytilitol		0	997 vs	963 s	—	902 w	—	833 vs	740 vs
Hydroxy*iso*-mytilitol		0	1003 vs	—	—	889 m	—	846 s; 840 s	733 s

TABLE 3. *Deoxy-derivatives of hexopyranose sugars.*

Compound	Frequencies (cm.$^{-1}$) of absorption peaks							
	Includes C–O–C vibrations	Type 1 ?	Type 2*b*	Other peaks	Type 2*c*	CH_2 rocking	Type 2*a*	Type 3
Tetrahydropyran	969 m	875 s	—	—	—	856 m	—	818 m
α-D-Glucopyranose	—	914 s	—	—	—	—	837 s	774 s
1 : 2 : 3 : 4 : 6-penta-*O*-acetyl-	942 vs; 935 vs; 911 s	905 s	—	886 m	—	—	841 s	743 m
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 vs; 914 w	896 w	—	884 w	—	—	842 w	745 w
β-D-Glucopyranose	—	909 m	896 vs	856 w *	—	—	—	—
2-deoxy-	968 s	906 s	891 s	—	—	868 vs	—	812 mbr
Methyl α-D-glucopyranoside	—	896 s	—	—	—	—	840 s	745 s
2-deoxy-	914 s	896 s	—	—	—	870 s	837 vs	760 s
Ethyl α-D-glucopyranoside								
2-deoxy-	938 m; 917 s	884 m	—	—	—	868 s	840 s	753 s
2 : 3-dideoxy-	921 m	888 m	—	—	—	866 m	841 vs	755 m; 735 s
Methyl α-D-mannopyranoside	972 s	914 w	—	—	888 w	—	843 m	808 s
3-deoxy-	972 vs; 950 s	—	—	—	881 w	855 m	838 m	814 s
Methyl β-D-galactopyranoside [a]	—	940 m	887 m	—	868 s	—	—	782 s
2-Deoxy-β-D-galactopyranose [b]	—	936 s	897 s	—	875 s	855 s	—	762 s
Methyl α-D-galactopyranoside	—	923 s	—	—	868 s	—	818 vs	784 vs
2-deoxy-	—	933 s	—	—	884 m	868 m	817 s	769 w; 735 s

* Possibly due to a trace of the α-anomer. [a] Also 821 cm.$^{-1}$ (vw). [b] Also 808 cm.$^{-1}$ (s).

J., 1952, 686), and in each case comparison is made with the spectra of the two hexahydroxy*cyclo*hexanes (generic name, " inositols ") which result when the methylene group is replaced by the grouping CH(OH). Each quercitol shows a strong peak at *ca.* 853 cm.$^{-1}$ which is not displayed by the corresponding inositols; a similar peak is given by the two quercitol penta-acetates examined, but not by *scyllo*inositol hexa-acetate. For all five compounds containing the ring methylene group, the peak has a mean frequency of 853 cm.$^{-1}$ with a small standard deviation of ± 6.

Although it is hoped to deal with other aspects of the spectra of these and other cyclitols in a future publication, it is interesting to note that some of the compounds listed in Tables 1 and 2 give rise to an absorption peak at 895 ± 6 cm.$^{-1}$, which seems to correspond to the type 1 vibration in the hexopyranose series [α-glucopyranoses, 917 ± 12; β-glucopyranoses, 920 ± 5 cm.$^{-1}$ (Part I)], and is possibly due to a ring vibration. Likewise they show bands at *ca.* 750 cm.$^{-1}$, which may well be the counterparts of the type 3 vibrations of hexopyranoses [glucopyranoses, 753 ± 17; galactopyranoses, 752 ± 20; mannopyranoses, 791 ± 18 (Part II)], and are possibly ring breathing frequencies. It is particularly interesting that the peak at 873 ± 11 cm.$^{-1}$ (Tables 1 and 2) is shown only by those compounds with equatorial hydrogen atoms [the chair form with the greater number of equatorial oxygen atoms is assumed (cf. Hassel and Ottar, *Acta Chem. Scand.*, 1947, **1**, 929)], since the type 2*c* peaks in galactose (871 ± 7 cm.$^{-1}$) and mannose (876 ± 9 cm.$^{-1}$) derivatives were attributed (Part II) to deformation of equatorial C–H bonds. Indeed this excellent agreement between configurations and spectra offers general support for the accepted structures of the cyclitols examined and affords a useful method of resolving future structural problems in this field.

(b) *In hexopyranoses.* Comparison of the spectra of 2- and 3-deoxyglucopyranose derivatives with those of closely related compounds which do not possess a methylene group (Table 3) clearly reveals that the deoxy-compounds give an additional peak at 867 ± 2 cm.$^{-1}$; this peak is of moderate or strong intensity for the free sugars or their glycosides. Similarly, an extra peak is encountered in the spectra of methyl 3-deoxy-α-D-mannopyranoside, 2-deoxy-β-D-galactopyranose, and methyl 2-deoxy-α-D-galactopyranoside (Table 3), but in these cases the situation is complicated by the presence of a type 2*c* peak. However, it seems that infra-red spectra could be usefully employed to distinguish deoxysugars (for 6-deoxy-sugars see below), special care being necessary when there is a possibility that the methylene group replaces a CH(OH) group having the hydrogen atom equatorial.

(c) *Assignment.* There can be little doubt that the peaks at 853 ± 6 cm.$^{-1}$ in quercitols and at 867 ± 2 cm.$^{-1}$ in 2- and 3-deoxyglucopyranose derivatives arise from ring-methylene groups. Burket and Badger (*loc. cit.*) assigned a similar frequency (856 cm.$^{-1}$) to a rocking mode involving all five methylene groups in tetrahydropyran. The fact that no analogous peak is present at 850—870 cm.$^{-1}$ in the spectra of D-xylopyranose derivatives in general (Part II), in spite of the fact that a ring-methylene group is present at position 5, suggests that a single methylene group next to the oxygen atom in the pyranose ring may absorb at a different frequency from a ring-methylene group in another position. Indeed there is a precedent for this, as Burket and Badger (*loc. cit.*) have suggested that overlapping of the van der Waals radii of the polar hydrogens of the methylene groups, which is enhanced when these are situated on either side of the ring oxygen, by virtue of the short C–O bond length, causes the increase in one of the methylene rocking vibrations from 856 cm.$^{-1}$ in tetrahydropyran to 1052 cm.$^{-1}$ in 1 : 4-dioxan. Absorption peaks at 933, 938, and 935 cm.$^{-1}$ in the spectra of α-D-xylopyranose, methyl α-D-xylopyranoside, and methyl β-D-xylopyranoside, respectively, which are not shown by the corresponding derivatives of glucopyranose, must also be considered for a rocking methylene frequency, but no convincing assignment can yet be made because, although other pentopyranoses absorb in this region, so do many of the corresponding hexopyranose derivatives; the difficulty arises mainly because other vibrations, including C–O stretchings, lead to absorption in this frequency range.

C-Methyl Groups.—(a) *In cyclitols.* In Table 2 the spectra of two cyclitols containing single *C*-methyl groups are compared with those of related cyclitols in which the *C*-methyl groups are replaced (*a*) by hydrogen atoms and (*b*) by *C*-hydroxymethyl groups. In each case there is a strong peak at 963 cm.$^{-1}$ which is not shown by the reference compounds. Similar comparisons of spectra between methyl*cyclo*hexane and *cyclo*hexane, between 1 : 1-dimethyl*cyclo*hexane and *cyclo*hexane, between *trans*-1 : 2-dimethyl*cyclo*hexane and *trans-cyclo*hexane-1 : 2-diol, and between *cis*-1 : 2-dimethyl*cyclo*hexane and *cis-cyclo*-

hexane-1 : 2-diol, reveal a strong additional peak in each *C*-methyl compound at *ca.* 967 cm.$^{-1}$ (respective values, 967, 962, 966, 977 cm.$^{-1}$) (cf. American Petroleum Institute Research Project No. 44). Thus in six cases the appearance of an absorption peak at 967 ± 6 cm.$^{-1}$ can be correlated with the introduction of a *C*-methyl group into a *cyclo*hexane derivative.

(b) *In hexopyranoses.* All seven 6-deoxy-derivatives of mannose or galactose so far examined (Part II) give an absorption peak near 967 cm.$^{-1}$. It would be unwise, however, to attempt to use this frequency for the identification of 6-deoxy-sugars, because confusion with frequencies attributable to the in-phase C–O stretching mode of ethers and esters is probable.

(c) *Assignment.* The assignment of *C*-methyl rocking frequencies in paraffins has provoked much discussion (cf. Sheppard and Simpson, *loc. cit.*) owing to the fact that vibrations of the same symmetry class involving the methyl rocking mode and skeletal vibrations may become mixed. However, the methyl rocking mode (in-plane, asymmetrical) of *n*-propane has been assigned to 923 cm.$^{-1}$; and the 2-methyl derivatives of pentane, heptane, octane, and nonane all show infra-red absorption at 950—961 cm.$^{-1}$, which has been ascribed to either C–C stretching or methyl rocking (Sheppard and Simpson, *loc. cit.*). It appears therefore that the assignment of one of the *C*-methyl rocking modes in simple derivatives of *cyclo*hexane, in cyclitols, and probably also in 6-deoxyhexopyranoses, to the absorption band appearing at *ca.* 967 cm.$^{-1}$ is reasonable.

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