882. *Infrared Spectra of Carbohydrates. Part VIII.* Hydropyranols and Hydrofuranols.*

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Assignments are suggested (Table 1) for the majority of fundamental frequencies of tetrahydropyran-2-, -3-, and -4-ol, and tetrahydro-2-hydroxymethylpyran, as well as (Table 2) for tetrahydrofuran-2- and -3-ol and tetrahydro-2-hydroxymethylfuran.

Since the complex spectra of sugars are only to be fully understood in relation to the spectra of simpler related molecules the spectra of some monohydroxy-derivatives of tetrahydropyran and tetrahydrofuran have been studied. The assignments of fundamental frequencies suggested here have been based on those for the parent rings tetrahydropyran [1,2] and tetrahydrofuran.[3,4] The assignments of other saturated rings including cyclohexane,[2,5,6] 1,4-dioxan,[2,7] 1,3,5-trioxan,[1,8,9,10] cyclopentane,[3,11] and 1,3-dioxolan [12] have also proved helpful. The new molecules discussed are all asymmetric with the exception of tetrahydropyran-4-ol, which has a plane of symmetry. All frequencies are permitted in both the Raman and the infrared spectra and the selection rules are of little value.

The suggested assignments for the tetrahydropyran derivatives are given in Table 1 which also includes a remeasurement of tetrahydropyran. The assignment of this follows Burket and Badger [2] fairly closely and the remaining assignments follow by analogy. A few points deserve special mention.

Tetrahydropyranols.—C–H *stretching vibrations.* The interaction is likely to be such that the carbon–hydrogen stretchings are to be classified as symmetrical and antisymmetrical CH_2 frequencies, rather than as equatorial and axial C–H stretches. The antisymmetrical modes are assigned to the higher frequencies since those below 2800 cm.$^{-1}$

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* Part VII, Barker, Bourne, Pinkard, and Whiffen, *Chem. and Ind.*, 1958, 658.

[1] Kahovec and Kohlrausch, *Z. phys. Chem.*, 1937, *B*, **35**, 29.
[2] Burket and Badger, *J. Amer. Chem. Soc.*, 1950, **72**, 4397.
[3] Tschamler and Voetter, *Monatsh.*, 1952, **83**, 303, 1228.
[4] Barrow and Searles, *J. Amer. Chem. Soc.*, 1953, **75**, 1175.
[5] Ramsay and Sutherland, *Proc. Roy. Soc.*, 1947, *A*, **190**, 245.
[6] Beckett, Pitzer, and Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2488.
[7] Ramsay, *Proc. Roy. Soc.*, 1947, *A*, **190**, 562.
[8] Stair and Nielsen, *J. Chem. Phys.*, 1957, **27**, 402.
[9] Ramsay, *Trans. Faraday Soc.*, 1948, **44**, 289.
[10] Decius, Steele, and Snyder, *J. Chem. Phys.*, 1951, **19**, 806.
[11] Miller and Inskeep, *J. Chem. Phys.*, 1950, **18**, 1519.
[12] Barker, Bourne, Pinkard, and Whiffen, *J.*, 1959, 802.

Table 1. *Assignments (cm.$^{-1}$) for tetrahydropyran derivatives.*

	Tetrahydropyran		Tetrahydropyran-2-ol	Tetrahydropyran-3-ol	Tetrahydropyran-4-ol		Tetrahydro-2-hydroxymethylpyran
Assignment	I.R.	Raman	I.R.	I.R.	I.R.	Raman	I.R.
OH Stretch	—	—	3395vs	3395vs	3350vs	—	3400vs
CH$_2$ antisymmetrical stretch		2957vs bd				2979vs bd	
		2929vs bd	2940vs	2940vs		2926vs bd	
	2910vs	2900w bd			2910vs		2910vs
		2849vs bd	2850s			2873vs bd	
	2815vs	2790vw		2810vs	2825vs	2835vs bd	2827vs
CH$_2$ symmetrical stretch	2735m	2753 m sh P	2730w	2730w	2740w		
	2700w	2712w sh PP		2700w	2690w		2710w
		2672w PP	2670w		2675w		
		2644w sh PP					
		2603m sh P				2603vw sh P	
CH$_2$ scissors	1470m		1475w	1475m	1474m	—	1467w
	1455s	1456s d	1463m	—	1452s	1460m b	1457m
	1445vs	—	1449s	1448s	—		1446s
	—	1433s d	—	—	1435w	1431m b	—
	1386s	1384w	1389m	1387w	1385m		1383m
C–H deformation	—	—	1425w	1420w	1425m	—	1415m
CH$_2$ wagging (* coupled with C–OH deformation)	1363w	—	1361s	1370m	1370s	—	1356m
	1352m	1348w	—	—	1354vw	1361w	—
	—	—	—	—	1318vw	—	—
	1303s	1299m	1300m*	1300s*	1300m*	1306w*	1255vw*
	1275s	1272m	1280m	—	1280s	1276m	1274s
C–H deformation		—	1334w	1335w	1338w	—	1325vw
CH$_2$ twisting	1260m	—	1263m	1258m	—	—	1268w
	—	1246m	1247vw	—	1245w	1240w	—
	—	—	—	1212s	1228vs	—	1224m
	1197vs	1197m	1201s	1198m	1185w	—	1208s
	—	1171m	1175s	1178m	1168m	1165vw	1183m
CH$_2$ (rock?)	1160m	1157m	1141s	1147s	1130vs	1132m bd	1160w
Ring frequencies (* coupled with C–O stretching of C–OH)	1093vw	1100vw	1080vs	1097vs	1082vs	—	1095vs
	1047vs	1049s	1057m	1069m	1065m	1072s b	1075m
	1030s	1019s	1030s*	1032m*	1035m*	—	1050vs*
	1013m	1009s	1018s	998s	1010s	1008m sh	1005m
C–OH deformation	—	—	981vs	983w	993s 987m	990vw	992m
CH$_2$ rock	970s	—	—	965s	963m	—	962w
Ring	873vs	873w	869s	874m 863m	863vs	—	872m
CH$_2$ rock...............	856m	852w	842m	846m	863vs	—	858s
Ring	817s	817vs sh PP	820m	803m	815s	815 vs sh PP	800m
CH$_2$ rock	—	759m PP	760vw	—	750m	723vw	—
Frequencies not assigned			1118m		908w		947m
	707m	715vw sh P	1095w	927w	885?		932w
	562s		937m	915s	800?	789w	920vw
	500w	458w b	917s	766w	703?		896s
	429m	431w b	903s	710m	685w	683w	837w
		403w b	806s	586s	610vs	614m sh P	830w
			701m	496m	522?	558vw	722w
		$\sim$250vw	635w	480w	466?	483s	703m
			532m	427m		415vw	576s
			429w			166vw	565w
							552m
							494w
							478w?
							451w?
							436w?

v, very; s, strong; m, medium; w, weak; P, polarised; PP, partially polarised; b, broad; d, diffuse; sh, sharp.

TABLE 2. *Assignments (cm.$^{-1}$) for tetrahydrofuran derivatives.*

Assignment	Tetrahydrofuran		Tetrahydrofuran-2-ol	Tetrahydrofuran-3-ol	Tetrahydro-2-hydroxymethylfuran
	I.R.	Raman	I.R.	I.R.	I.R.
OH stretch	—	—	3400vs	3380vs	3400vs
CH_2 antisymmetric stretch	2981vs	2970s b			
	—	2962s P	2955vs		
	2947w	—		2950vs	
	2933w	2934m sh P			2930vs
CH_2 symmetric stretch	2878s	2876s sh P	2890vs	2870vs	
	2868s	2863s sh P			2855vs
			2720w	2720w	
				2680w	
CH_2 scissors		1489m b	1495vw	1490w	1495vw 1490vw
	1462vs	—	1469s	1470w	1470s
		1449m b	1451m	1450s	1462w
					1455m
C–H deformation	—	—	1432m	1431m	1430vw
CH_2 wagging (* coupled with C–OH deformation)	1366s	1368vw	1373s	1375w	1368m
	1332w	1335vw	1345m	1338s	1338w
	1286s	—	1275s*	1295m*	1292w*
C–H deformation	—	—	1330m?	1350vw?	1308w
CH_2 twisting	—	—	—	1258w	1250m
	1233s	1238m b	1245m	1235m	1230m
	1181s	1173vw	1190s	1208w	1190s
C–OH stretch	—	—	1123s	1125s	1110m
Ring vibrations	1069vs	1073vw	1068vs	1075vs	1075vs
	1031s	1029ms	1040vs	1052m	1055vs
C–OH deformation	—	—	990vs	973s	990s
Ring vibration	911vs	914vs P	923vs	903vs	928s
CH_2 rocking	—	857w	852s	860m	857m
	761vw	—	760m	773s	773s
Ring vibrations		650vw			
		595vw			
Not assigned	834vw	811vw		1002s	1420vw
	824vw				1415m
					1387w
					1002vw
					904w
					882m
					819s

Symbols: see Table 1.

show appreciably polarised Raman lines and this is in accord with their relative magnitude in hydrocarbons.[13]

Methylene scissoring vibrations. Burket and Badger[2] have assigned the infrared absorption at 1451 and 1381 cm.$^{-1}$ to the scissoring vibrations of the methylene groups in tetrahydropyran. In the present work the infrared absorption peak near 1451 cm.$^{-1}$ was resolved into two absorptions with maxima at 1455 and 1445 cm.$^{-1}$ respectively. In addition a peak was found at 1470 cm.$^{-1}$. Tetrahydropyran should have, theoretically, five methylene scissoring vibrations and the frequencies assigned to these are shown in Table 1. Three of the methylene groups are of the type C–CH_2–C, and three of the assigned frequencies are close to the frequency range of these vibrations in cyclohexane (1443—1456 cm.$^{-1}$). The enhanced frequency 1470 cm.$^{-1}$ may be expected for a methylene group attached to one oxygen and one carbon atom. In the tetrahydropyranols frequencies similar to those for tetrahydropyran have been allocated to the methylene scissoring vibrations except that only a maximum of four such frequencies is found as may be predicted.

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[13] Sheppard and Simpson, *Quart. Rev.*, 1953, **7**, 19.

Methylene wagging and twisting vibrations. The wagging frequencies in the range 1272—1370 cm.$^{-1}$ and the twisting frequencies in the range 1165—1268 cm.$^{-1}$ are assigned with less certainty. Some support is obtained by a comparison of the infrared spectra of β-D-ribopyranose and β-L-arabopyranose with those of 2-deoxy-β-L-ribopyranose and 1-deoxy-L-arabopyranose respectively. The 2-deoxy-β-L-ribopyranose with its extra ring-methylene group has extra peaks at 1293 cm.$^{-1}$ (CH_2 wagging) and 1194 cm.$^{-1}$ (CH_2 twisting) while 1-deoxy-L-arabopyranose has extra peaks at 1294 (CH_2 wagging) and 1214 cm.$^{-1}$ (CH_2 twisting). In comparisons of corresponding hexose and deoxyhexose derivatives, where the position is necessarily more complex because of the methylene of the hydroxymethyl group, the new twisting frequency in the deoxy-derivative could not be located. However, new absorption peaks in the spectra of 2-deoxy-β-D-galactopyranose (1344 cm.$^{-1}$) and 1,2-dideoxy-D-galactopyranose (1349 cm.$^{-1}$), which are not shown by α-D-galactopyranose, probably arose from wagging vibrations. Similar comparisons of D-glucose and deoxy-D-glucose derivatives permitted the allocation of wagging frequencies in the range 1272—1370 cm.$^{-1}$.

Methylene rocking vibrations. The assignments for these vibrations follow closely those suggested by Burket and Badger [2] for tetrahydropyran. One of these rocking vibrations, that near 856 cm.$^{-1}$, has been previously allocated by some of us [14] to the methylene rocking vibrations of 2- and 3-deoxy-sugars and of the methylene-containing cyclitols. Some support for the allocation of a frequency near 750 cm.$^{-1}$ to a methylene rocking vibration comes again from comparisons of pentoses and deoxypentoses. Neither the absorption at 753 cm.$^{-1}$ (1-deoxy-L-arabopyranose) nor that at 756 cm.$^{-1}$ (2-deoxy-β-L-ribopyranose) has any counterpart in the spectra of the corresponding pentose although in the former case this may be coupled with the ring breathing vibration. Other deoxypyranose derivatives showing absorption here are 1,2-dideoxy-D-galactopyranose, 755 cm.$^{-1}$, and ethyl 2,3-dideoxy-α-D-glucopyranoside, 735 and 755 cm.$^{-1}$.

C–H *deformation vibrations.* Previous deuteration studies by some of us [15] have firmly established that the two lone C–H deformations for a hydrogen on $C_{(1)}$ of an unsubstituted hexopyranose or pentopyranose occur in the ranges 1340—1387 and 1275—1340 cm.$^{-1}$. In the present study allocations were made in the ranges 1415—1425 and 1325—1338 cm.$^{-1}$. In both frequency ranges there was no corresponding absorption exhibited by tetrahydropyran.

Ring vibrations. The frequencies at 817 cm.$^{-1}$ in tetrahydropyran and at 815 cm.$^{-1}$ in tetrahydro-4-hydroxypyran are assigned to the symmetric ring breathing vibration since in both cases these are the strongest Raman lines below 1500 cm.$^{-1}$ and both are highly polarised. The infrared band at 873 cm.$^{-1}$ in tetrahydropyran and near this frequency in all the derivatives is believed to correspond with the type I absorption of the aldopyranose sugars.[16] This ring vibration was considered by Burket and Badger [2] to include considerable contribution from the ring C–O–C antisymmetrical stretching. The remaining assignments for the ring vibrations follow closely those made by Burket and Badger [2] for tetrahydropyran.

Vibrations involving hydroxyl groups. The hydroxyl stretching frequencies are very characteristic and are easily identified at 3350—3400 cm.$^{-1}$. They have been discussed previously in hydrogen-bonding studies by Barker *et al.*[17] In order to confirm this assignment and locate the other frequencies associated with the C–OH group, deuterium-labelled derivatives (I and II) of tetrahydropyran-2-ol were prepared. Absorption peaks near 1300 and 1030 cm.$^{-1}$ in the spectra of tetrahydropyran-2-ol and the 3-deutero-compound (I) disappeared on deuteration of the hydroxyl, to give (II). Further, the intense absorption shown by tetrahydropyran-2-ol at 981 cm.$^{-1}$, which, it was suspected, included

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[14] Barker, Bourne, Stephens, and Whiffen, *J.*, 1954, 4211.

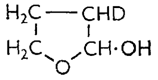
[15] Stacey, Barker, Bourne, Moore, Weigel, and Whiffen, 2nd United Nations Internat. Conference on the Peaceful Uses of Atomic Energy, 1958, No. 1466.

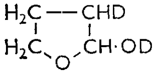
[16] Barker, Bourne, Stacey, and Whiffen, *J.*, 1954, 171.

[17] Barker, Brimacombe, Foster, Whiffen, and Zweifel, *Tetrahedron*, 1959, **7**, 10.

coupling with a CH_2 rocking mode, split into two peaks at 979s and 967m in the spectra of compound (I). The latter frequency persists as a weak absorption at 960 cm.$^{-1}$ in the

(I)





(II)

spectra of the dideutero-compound (II), but the former is absent. The deuterium-sensitive absorption at 981 cm.$^{-1}$ in tetrahydropyran-2-ol, which has strong counterparts in the spectra of the other alcohol derivatives, is therefore also believed to be associated with the C–OH group. The C–OH stretching (around 1030 cm.$^{-1}$) of 3-hydroxy-steroids [18] is probably the counterpart of the 1030 cm.$^{-1}$ absorption of tetrahydropyran-2-ol. Following Stuart and Sutherland,[19] we consider the peak at 1300 cm.$^{-1}$ to be probably the in-plane O–H deformation. In many cases coupling either with adjacent CH_2 groups or with ring vibrations is to be expected. In the case of tetrahydropyran-3-ol the extra peak at 1085 cm.$^{-1}$ may be due to the bonded OH.

Tetrahydrofuranols.—C–H stretching vibrations. The tetrahydrofuran ring, like that of cyclopentane, is probably almost planar with only a very small degree of puckering.[11] The C–H stretching vibrations of tetrahydrofuran are therefore to be regarded as symmetric and antisymmetric CH_2 stretchings as in the case of cyclopentane. In cyclopentane the symmetric vibrations [11] occur near 2870 cm.$^{-1}$. For tetrahydrofuran the two absorption peaks at 2878 and 2868 cm.$^{-1}$ are assigned to such vibrations since they are accompanied by strong polarised Raman lines as required for vibrations of this symmetry type. The weak absorption found at 2720 and 2680 cm.$^{-1}$ in tetrahydrofuran-2- and -3-ol is probably also of this type. The antisymmetric vibrations are found near 2966 cm.$^{-1}$ for cyclopentane. Tetrahydrofuran should show a maximum of four such vibrations, and the four frequencies from 2981 to 2933 cm.$^{-1}$ are assigned to these vibrations.

Methylene scissoring vibrations. Tschamler and Voetter [3] have assigned the Raman line at 1489 cm.$^{-1}$ to a scissoring vibration of tetrahydrofuran. The same assignment is made in Table 2, and it is suggested that it is concerned with the O–CH_2–C group since this frequency is very weak in the 2-hydroxy-derivative. The other two assignments are of frequencies nearer to the 1455 cm.$^{-1}$ scissoring vibrations of cyclopentane [11] and hence more concerned with the C–CH_2–C groups. In support of this the 1470 cm.$^{-1}$ band in the 3-hydroxy-compound is weak.

Methylene wagging vibrations. Miller and Inskeep [11] assigned frequencies 1316, 1283, and 1258 cm.$^{-1}$ to wagging modes in cyclopentane, and Tschamler and Voetter [3] tentatively assigned frequencies of 1367, 1338, 1290, and 1238 cm.$^{-1}$ to wagging modes in tetrahydrofuran. These assignments indicate that an oxygen atom again increases the frequency of the wagging vibration and it is probable that the 1367 cm.$^{-1}$ band arises from the O–CH_2–C groups. In Table 2, the lowest of the suggested frequencies, *i.e.*, 1238 cm.$^{-1}$, is assigned to a methylene twisting vibration.

Methylene twisting vibrations. In cyclopentane [11] frequencies of 1306, 1207, and 1033 cm.$^{-1}$, and in tetrahydrofuran [3] those of 1104 and 1180 cm.$^{-1}$, have been assigned to twisting vibrations. In the measurement of the spectra of tetrahydrofuran we failed to detect the 1104 cm.$^{-1}$ band and so have assigned the 1181 and 1233 cm.$^{-1}$ frequencies to methylene twisting vibrations.

Methylene rocking vibrations. Miller and Inskeep [11] have assigned the 1104, 964, and 896 cm.$^{-1}$ frequencies of cyclopentane to methylene rocking vibrations. Tschamler and Voetter [3] suggested 1031 and 964 cm.$^{-1}$ as suitable candidates for similar vibrations in tetrahydrofuran. We found no band at 964 cm.$^{-1}$ in the tetrahydrofuran spectra, nor was an analogous band present in the furanols. We have therefore assigned bands at 852—860 and 760—773 cm.$^{-1}$ to the methylene rocking vibration, since although these

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[18] Cole, Jones, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 5571.

[19] Stuart and Sutherland, *J. Chem. Phys.*, 1952, **20**, 1977; 1956, **24**, 559.

are weak in tetrahydrofuran itself they become moderately strong infrared bands in the furanols.

Ring vibrations. The frequency at 914 cm.$^{-1}$ in the tetrahydrofuran spectrum is assigned to the symmetric ring breathing vibration since it is the strongest polarised Raman line below 1500 cm.$^{-1}$. The frequency is somewhat higher, as expected, than that of the corresponding vibration of cyclopentane,[11] at 886 cm.$^{-1}$. The strong infrared bands at 1031 and 1069 cm.$^{-1}$ in the spectrum of tetrahydrofuran, with counterparts of similar intensity in the tetrahydrofuranol spectra, are believed to be due to ring vibrations. The other assignments to ring deformation vibrations, of the frequencies 595 and 650 cm.$^{-1}$ (at 545 and 617 cm.$^{-1}$ for cyclopentane), follow those of Tschamler and Voetter.[3]

C–H *deformations.* The assignment of the higher C–H deformation frequency follows closely that of the hydropyranols and clearly only arises for the hydrofuranols. The lower C–H deformation frequency appears somewhat weak and variable and can thus be assigned only tentatively.

Hydroxyl group vibrations. The OH stretching frequencies are easily assigned and require no comment. As found with the tetrahydropyranols a vibration associated with the C–OH group appears in the range 973—990 cm.$^{-1}$. Bands near 1110—1125 cm.$^{-1}$ probably correspond to the C–O stretching since this frequency generally increases as the ring size gets smaller.[20] A tentative assignment for the OH deformation has been made at 1275—1292 cm.$^{-1}$ by analogy with the pyranols.

EXPERIMENTAL

The preparation and physical constants of the hydroxy-derivatives of tetrahydropyran and tetrahydrofuran used have already been reported.[17]

Preparation of [3-^{2}H$_{1}$]*Tetrahydropyran*-2-[^{2}H]ol (II) and [3-^{2}H$_{1}$]*Tetrahydropyran-2-ol* (I).—Redistilled dihydropyran (1 g.) was shaken in a " dry box " with deuterium oxide (5 ml.) containing concentrated sulphuric acid (1 drop) until a homogeneous solution was obtained (3 hr.). After being kept for 1 hr., the mixture was neutralised with anhydrous potassium carbonate and distilled, to give [3-^{2}H$_{1}$]tetrahydropyran-2-[^{2}H]ol, b. p. 50°/0·1 mm. This product was dissolved in water (80 ml.), sodium hydrogen carbonate was added, and the solution was extracted continuously overnight with ether. After being dried (Na_2SO_4), the ether extract was fractionally distilled, to yield [3-^{2}H$_{1}$]tetrahydropyran-2-ol.

Measurement of Spectra.—Raman spectra were obtained as previously described.[12] The infrared spectra were measured in a Perkin–Elmer 21 double-beam spectrometer with a sodium chloride and a potassium bromide prism. The carbon–hydrogen and hydroxyl stretching frequencies were measured in the third order on a grating spectrometer having a 2500 lines/inch grating. The spectra were measured on liquid films.

Infrared spectrum of [3-^{2}H$_{1}$]*tetrahydropyran*-2-[^{2}H]*ol* (containing about 10% of [3-^{2}H$_{1}$]-tetrahydropyran-2-ol): 3420m (OH stretching impurity), 2950vs, 2865s, 2730w, 2670vw, 2510vs (OD stretching); 2220m, 2190w, 2170w, 2125w (C–D stretching); 1725w, 1470w, 1456m, 1442m, 1390m, 1382m, 1360m br, 1326w, 1306vw, 1282m, 1257m, 1235w, 1220w, 1205w, 1162m, 1147s br, 1090vs, 1072vs, 1062vs, 1020vs, 960w, 935w, 905m, 896s, 855s, 820m, 762m, 735m.

Infrared spectrum of [3-^{2}H$_{1}$]*tetrahydropyran-2-ol:* 3420vvs, (OH stretching), 2950vs, 2870s, 2740w, 2680vw, 2220m, 2190w, 2160w, 2120vw, 1725w, 1470w, 1461m, 1444m, 1387m, 1358m, 1334vw, 1300m, 1282m, 1257m, 1230w, 1215w, 1200m, 1170s, 1140s, 1135s, 1095w, 1076vs, 1060vs, 1028vs, 1015vs, 979s, 967m sh, 950vw, 935s, 902s, 895s, 870vs, 838vw, 822vs, 798m, 768s, 739m.

The authors thank Professor M. Stacey, F.R.S., for his interest. One of them (R. H. M.) thanks Glaxo Ltd. for the award of a scholarship. They are indebted to the British Rayon Research Association for the loan of a Raman spectrometer.

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[*Received, May 4th,* 1960.]

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[20] Zeiss and Tsutsui, *J. Amer. Chem. Soc.*, 1953, **75**, 897.