717. *A Proton Resonance Study of the Conformations of Carbohydrates in Solution. Part I. Derivatives of* 1,2-O-*Isopropylidene*-α-D-xylo-hexofuranose.

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The 60 Mc./sec. proton resonance spectra of thirteen 1,2-O-isopropylidene-α-D-*xylo*hexofuranose derivatives, each containing two *cis*-fused five-membered rings, are reported. For the first time complete assignments and analyses are given for the spectra of a related series of carbohydrates, and the chemical shifts of individual hydrogen atoms are shown to be characteristic of their position in the molecules. From a study of the coupling constants observed between neighbouring hydrogen atoms it is shown that, without exception in the molecules studied, the furanose ring adopts a " skew conformation " * with $C_{(2)}$ and $C_{(3)}$ displaced below and above the plane defined by the other ring atoms. Consequently the five-membered isopropylidene ring does not lock O, $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$ in one plane. Furthermore the five-membered anhydro-ring in 3,6-anhydro-1,2-O-isopropylidene-α-D-glucofuranose (XII) and its 5-O-tosyl derivative (XI) takes up an alternative " envelope conformation " * in which $C_{(4)}$ is alone displaced from the plane of the other four ring atoms whilst the furanose ring retains the " skew " form.

THE shapes of carbohydrate rings are of considerable importance in interpreting their chemical and physical properties but until recently no method has existed by which the conformations of ring compounds could be determined in solution. It has now been shown,[2] however, that proton magnetic resonance spectroscopy, which is well established as a powerful method for determining the detailed structure and stereochemistry of a molecule, can also yield precise information concerning its conformation. For this purpose, and for characterising the molecule, a full analysis of the proton magnetic resonance spectrum is essential. In the past the complexity of carbohydrate spectra has resulted in the detailed assignment and interpretation of comparatively few examples. However, specific conformations have been suggested for the D-ribofuranose ring of purine and pyrimidine nucleosides,[3] for thymidine,[4] and for certain deoxyribonucleosides[5] and nucleotides.[6] It seemed worthwhile therefore to investigate systematically a series of related compounds which might be expected to give spectra capable of full interpretation. From a consideration of the chemical shifts expected in the molecule, it appeared that derivatives of 1,2-O-isopropylidene-α-D-*xylo*hexofuranose might constitute such a series.

Observations on saturated molecules of known form[7,8] have suggested that the coupling constants observed in these compounds are largely dependent on the precise molecular geometry. This view has been supported by the theoretical studies by Karplus[9] who has suggested that the coupling constant (J) is related to the dihedral angle (ϕ) separating the relevant carbon–hydrogen bonds according to the equation

$$J = J_0 \cos^2 \phi - 0.28 \text{ c./sec.} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

* The term " skew conformation " is used here to denote a conformation analogous to the C_2 form of cyclopentane,[1] and the term " envelope conformation " to describe one analogous to the C_s form of cyclopentane.[1]

[1] Kilpatrick, Pitzer, and Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2483.
[2] Abraham, McLauchlan, Dalby, Kenner, Sheppard, and Burroughs, *Nature*, 1961, **192**, 1150.
[3] Jardetzky, *J. Amer. Chem. Soc.*, 1960, **82**, 229.
[4] Lemieux, *Canad. J. Chem.*, 1961, **39**, 116.
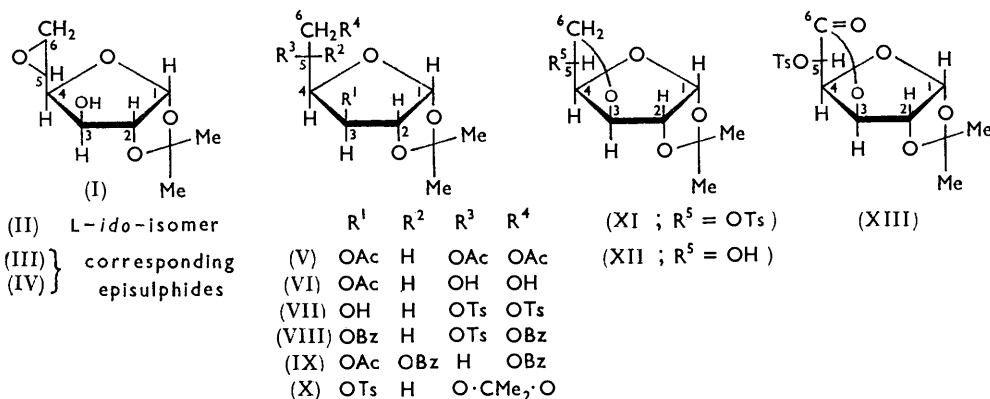[5] Jardetzky, *J. Amer. Chem. Soc.*, 1961, **83**, 2919.
[6] Jardetzky, *J. Amer. Chem. Soc.*, 1962, **84**, 62.
[7] Lemieux, Kullnig, Bernstein, and Schneider, *J. Amer. Chem. Soc.*, 1958, **80**, 6098.
[8] Anet, *Canad. J. Chem.*, 1961, **39**, 789.
[9] Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

where $J_0 = 8.5$ for $0° \leqslant \phi \leqslant 90°$ and 9.5 for $90° \ll \phi \leqslant 180°$. Since the dihedral angles observed in a cyclic compound are determined by the mode and extent of the buckling of the ring, this equation allows the conformation of the ring in solution to be calculated from the observed coupling constants. In practice, however, it appears that, whilst equation (1) gives the form of the angular dependence of the coupling constants, different systems require different parameters to yield consistent and reasonable results.[8,10,11] This makes the significance of the equation difficult to assess and of necessity causes some uncertainty in the conclusions deduced from its use. It is important to realise, however, that considerable information on the conformation of a ring compound can be obtained from the experimental observation that coupling constants are functions of molecular geometry. Thus symmetry in ring buckling is reflected in an equality of certain coupling constants, as has already been shown for one five-membered ring compound.[12]

	R¹	R²	R³	R⁴
(V)	OAc	H	OAc	OAc
(VI)	OAc	H	OH	OH
(VII)	OH	H	OTs	OTs
(VIII)	OBz	H	OTs	OBz
(IX)	OAc	OBz	H	OBz
(X)	OTs	H	O·CMe₂·O	

(I)   Me
(II) L-*ido*-isomer
(III) ⎫ corresponding
(IV) ⎭ episulphides
(XI ; R⁵ = OTs)
(XII ; R⁵ = OH)
(XIII)

It is important to note that in the above formulæ, in particular the 3,6-anhydro-derivatives (XI), (XII), and (XIII), the configurations shown for carbon-5 denote their relationship to D- and L-glyceraldehyde since the formulæ are derived from Fischer projections. Conformational and steric relationships are not therefore implied.

The work described here was initiated therefore to characterise the proton magnetic resonance spectra of some known 1,2-*O*-isopropylidene-α-D-*xylo*hexofuranose derivatives and to determine the conformation of the furanose ring in each of them. It represents the completion of an investigation previously reported in preliminary form.[13]

All thirteen compounds (I—XIII) investigated yield complex spectra, some of which are shown in the Figures. Fig. 1a represents the spectrum of 5,6-dideoxy-5,6-epithio-1,2-*O*-isopropylidene-α-L-idofuranose [14] (IV), Fig. 1b that of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose [15] (V), and Fig. 2a that of 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose [16] (XII). Full analysis of the spectra is possible in all cases except for those of 3-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose [17] (VI) and of 1,2:5,6-di-*O*-isopropylidene-3-*O*-tosyl-α-D-glucofuranose [18] (X). The data obtained are summarised in Tables 1 and 2. Included in Table 1 is one set of values obtained with the 3,5,6 tri-*O*-acetyl derivative (V) in solution in chloroform. This shows that little change in chemical shift occurs in this solvent.

[10] Lenz and Heeschen, *J. Polymer. Sci.*, 1961, **51**, 247.
[11] Abraham and McLauchlan, *Mol. Phys.*, in the press.
[12] Abraham and McLauchlan, *Mol. Phys.*, 1962, **5**, 195.
[13] Abraham, McLauchlan, Hall, and Hough, *Chem. and Ind.*, 1962, 216.
[14] Hall, Hough, and Pritchard, *J.*, 1961, 1537.
[15] Ohle and Spencker, *Ber.*, 1926, **59**, 1836.
[16] Ohle, Vargha, and Erlbach, *Ber.*, 1928, **61**, 1211.
[17] Josephson, *Annalen*, 1929, **472**, 217.

Peak assignment is normally straightforward except in the spectra of compounds containing one or more hydroxyl groups where the hydroxyl-hydrogen peaks obscure those due to ring hydrogens. Addition of a trace of acid simplifies the spectra by shifting
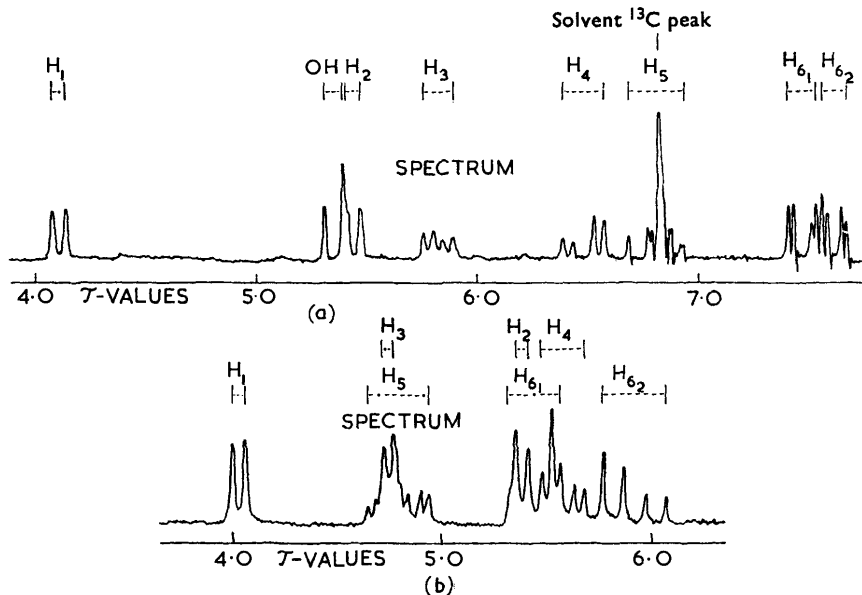
FIG. 1. The 60 Mc./sec. proton magnetic resonance spectra of (a) 5,6-dideoxy-5,6-epithio-1,2-*O*-isopropylidene-α-L-idofuranose (IV) and (b) 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (V). The peaks due to methyl and solvent are not shown.
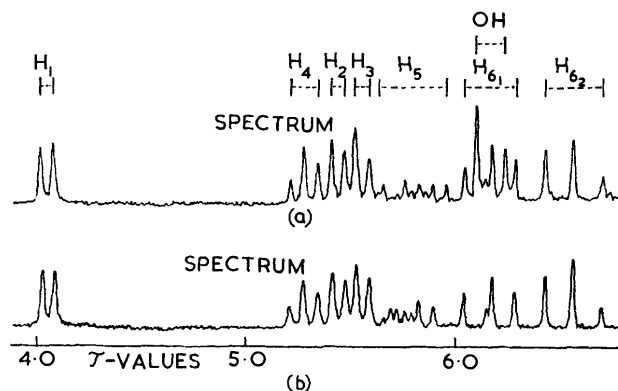
FIG. 2. The 60 Mc./sec. proton magnetic resonance spectrum of 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose (XII), (a) in neutral solution, (b) with added acid. The peaks due to methyl and solvent are omitted.

the hydroxyl hydrogen peaks and removing any coupling between these hydrogens and adjacent ring ones. This effect is shown in Fig. 2b and allows identification of the ring hydrogen atoms by normal means.

In all the spectra, the doublet due to $H_{(1)}$ occurs at lower field (τ value) than any of

6 D

TABLE 1.

Proton chemical shifts (τ values).

Compound	1H	2H	3H	4H	5H	6_1H	6_2H	OH	Me$_2$C		
(I)	4·06	5·44	5·76	6·27	6·78	7·17	7·26	5·66	8·60	8·72	
(II)	4·06	5·48	5·74	6·38	6·86	7·23	7·34	5·42	8·62	8·73	
(III)	4·09	5·46	5·88	6·48	6·88	7·39	7·64	5·30	8·62	8·72	
(IV)	4·11	5·45	5·83	6·44	6·86	7·49	7·63	5·36	8·65	8·75	
(V)	4·04	5·39	4·76	5·59	4·81	5·51	5·94	—	8·53	8·71	
(V) [b]	4·06	5·49	4·64	5·58	4·77	5·39	5·84		8·46	8·67	
(VI)	4·11	5·44	4·79	5·79	[a]	[a]	[a]	[a]	8·64	8·72	
(VII)	4·18	5·49	5·79	5·18	4·80	5·67	5·98	5·68	8·66	8·79	tosyl Me: 7·51 tosyl: 2·33
(VIII)	3·99	5·28	4·73	5·39	4·59	5·23	5·50	—	8·51	8·70	phenyl: 1·90 —2·90 tosyl Me: 7·41
(IX)	4·14	5·44	4·36	5·36	4·30	5·32	5·68	—	8·56	8·75	phenyl: 2·00 —2·84
(X)	4·00	5·17	5·25		[c]			—	8·57, 8·69, 8·86		tosyl Me: 7·52 tosyl: 2·30
(XI)	4·06	5·45	5·54	5·27	4·98	6·37	6·90	—	8·63	8·72	tosyl Me: 7·51 tosyl: 2·47
(XII)	4·06	5·45	5·58	5·28	5·78	6·19	6·56	6·14	8·57	8·70	
(XIII)	3·99	5·13	5·02	5·10	4·38	—	—	—	8·58	8·69	tosyl Me: 7·56 tosyl: 2·30

[a] Broad complex: 6·05—6·60. [b] Chloroform solution. [c] Broad complex: 5·86—6·29.

the other ring hydrogens because of the proximity of this atom to two oxygen atoms. From the splitting of this doublet, the atom $H_{(2)}$ to which $H_{(1)}$ couples is identified. As can be seen from Table 2, the coupling between $H_{(2)}$ and $H_{(3)}$ is very small and results in the spectral patterns of each of these hydrogen atoms being doublets. It so happens that in some of the molecules studied, 3,6-anhydro-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-gluco-furanose [16] (XI) and the other 3,6-anhydro-glucofuranose derivative (XII), the coupling constants $J_{1,2}$ and $J_{3,4}$ are so nearly equal that $H_{(2)}$ and $H_{(3)}$, which have very similar

TABLE 2.

Proton coupling constants (c./sec.).

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6_1}$	$J_{5,6_2}$	$J_{6_1,6_2}$	$J_{3,OH}$
(I)	3·6	<0·5	2·7	6·9	4·0	2·1	5·4	5·0
(II)	3·7	<0·5	2·9	6·7	4·3	2·5	5·2	5·1
(III)	3·7	<0·5	2·8	8·6	5·8	5·1	0·9	5·2
(IV)	3·7	<0·5	2·8	8·5	6·1	5·2	1·3	5·2
(V)	3·5	<0·5	3·0	9·0	2·0	6·3	12·3	—
(VI)	3·7	<0·5	2·8	8·2	[a]	[a]	[a]	[a]
(VII)	3·6	<0·5	3·3	6·5	1·6	6·1	11·3	—
(VIII)	3·7	<0·5	2·8	7·8 [b]	2·0	5·8	13·0	—
(IX)	3·7	<0·5	3·3	7·0	2·8	7·6	12·4	—
(X)	3·8	<0·5	1·7 [d]	[c]	[c]	[c]	[c]	—
(XI)	3·5	<0·5	3·7	4·1	6·5	8·1	8·7	—
(XII)	3·6	<0·5	3·9	3·9	6·1	8·1	8·1	[e]
(XIII)	3·6	<0·5	2·7 [b]	4·1	—	—	—	—

[a] Broad complex. [b] From chloroform spectrum. Broad complex. [d] Broad lines; value may be low. [e] $J_{5,OH}$ 8·1 c./sec.

chemical shifts, cannot be differentiated, and peak assignment by normal means is not possible. Furthermore two other compounds, the 1,2:5,6-di-*O*-isopropylidene-3-*O*-tosyl derivative (X) and 1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-glucofuranurono-6 ⟶ 3-lactone (XIII), yield spectra which, whilst not having nearly equal values of $J_{1,2}$ and $J_{3,4}$, are so complex that normal identification of $H_{(2)}$ is not possible. Each of these problems is overcome by the technique of double irradiation.[19] Thus, if a strong radiofrequency field is

[18] Jones, *Canad. J. Chem.*, 1956, **34**, 310.
[19] Abraham, Freeman, McLauchlan, and Hall, *J.*, 1962, 2080.

applied near the resonance frequency of a particular hydrogen atom, the spin coupling to a second group can be destroyed. If this group has a doublet resonance pattern it then collapses to a single line. Consequently, irradiation of the $H_{(1)}$ doublet in these compounds results in the collapse of the $H_{(2)}$ doublet which is thus identified.

Inspection of Table 1 shows that the τ-value of $H_{(1)}$ (4·07 ± 0·1) is constant and is characteristic of this hydrogen atom. The chemical shift of $H_{(2)}$ (5·45 ± 0·1) is also constant for those compounds which have a 3-hydroxy- or 3-acetoxy-substituent or which, with the exception of the 5-*O*-tosyl-glucofuranuronolactone (XIII) which shows many unusual values, contain a 3,6-anhydro-bridge. As can be seen, for example, by comparison of the values obtained from 1,2-*O*-isopropylidene-5,6-di-*O*-tosyl-α-D-glucofuranose [20] (VII) and 3,6-di-*O*-benzoyl-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-glucofuranose [21] (VIII), the τ-value of this hydrogen atom is changed only when the 3-substituent contains a phenyl residue. This suggests that it is subject to a local magnetic field due to ring current effects. For a given 3-substituent, the τ-value of $H_{(3)}$ is also constant although exceptions are found in the case of 3-*O*-acetyl-5,6-di-*O*-benzoyl-1,2-*O*-isopropylidene-α-L-idofuranose [22] (IX), which may be due once more to ring current effects in phenyl residues and in the 5-*O*-tosylglucofuranuronolactone derivative (XIII) which is again anomalous. The atypical chemical shifts observed in the latter compound are probably a result of the diamagnetic anisotropy of the carbonyl group. All the other hydrogen atoms possess chemical shifts which are either constant when the *O*-substituent is the same or which vary according to the proximity of groups causing local variations in the magnetic field experienced by the hydrogen atom.

The coupling constants observed in the epoxide rings of 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose [23] (I) and 5,6-anhydro-1,2-*O*-isopropylidene-α-L-idofuranose [24] (II) agree quite well with those of previous workers [25,26] and contrast with the novel, very small, *gem* coupling constants observed in the episulphide rings of 5,6-dideoxy-5,6-epithio-1,2-*O*-isopropylidene-α-D-glucofuranose [14] (III) and the epithio-L-idofuranose derivative (IV). The chemical shifts and coupling constants together observed for hydrogen atoms in epoxide and episulphide rings are completely characteristic of these groupings and may be used to diagnose them.

As can be seen from Table 2, the value of $J_{1,2}$ is constant throughout the series of compounds, which implies that the isopropylidene link between ring atoms $C_{(1)}$ and $C_{(2)}$ maintains the ring oxygen, $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$ in fixed juxtaposition. The magnitude of the coupling constant observed between eclipsed hydrogen atoms in the camphane-*cis*-2,3-diols [8] is known to be *ca.* 7·7 c./sec. Consequently the coupling constant $J_{1,2}$ (3·65 ± 0·2 c./sec.) observed in these compounds clearly demonstrates that $H_{(1)}$ and $H_{(2)}$ are not eclipsed. Thus the function of the isopropylidene group, whilst determining the configuration of the part of the molecule to which it is attached, is not to cause O, $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$ to become coplanar. The formation of an *O*-isopropylidene derivative of *cis* axial-equatorial hydroxyl groups on adjacent carbon atoms of the chair form of a six-membered ring requires the projected valency angle between these hydroxyl groups to be reduced to less than 60°.[27,28] Such a change would lead to a partial flattening of the chair conformation, since the four ring-atoms associated with the *O*-isopropylidene group now tend towards coplanarity. It has been postulated that the isopropylidene ring is planar and that the six-membered ring consequently adopts a half-chair conformation

[20] Ohle and Dickhauser, *Ber.*, 1925, **58**, 2593.
[21] Ohle, *Ber.*, 1929, **62**, 2885.
[22] Vargha, *Ber.*, 1934, **67**, 1224.
[23] Ohle and Vargha, *Ber.*, 1929, **62**, 2435.
[24] Meyer and Reichstein, *Helv. Chim. Acta*, 1946, **29**, 159.
[25] Reilly and Swalen, *J. Chem. Phys.*, 1960, **32**, 1378.
[26] Musher, *Mol. Phys.*, 1961, **4**, 311.
[27] Angyal and McDonald, *J.*, 1952, 686; Mills, *Adv. Carbohydrate Chem.*, 1955, **10**, 21.
[28] Hough and Richardson, *J.*, 1961, 5561.

analogous to those of cyclohexene [29] and its oxide.[30]   By analogy an isopropylidene ring fused to a furanose ring would be expected to give a conformation in which the projected valency angle between the bridgehead hydrogens, and hence the oxygens attached to the isopropylidene group, approaches zero.   Our findings show that this angle is in fact *ca.* 50° [calculated from equation (1) with the parameters given below] in all of the 1,2-*O*-iso-propylidene-α-D-xylofuranoses examined, and hence does not cause O, $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$ to attain a planar configuration.   This evidence does not, therefore, support the view that an isopropylidene substituent deforms a pyranose chair to a half-chair, and the proton magnetic resonance spectra of such derivatives are in agreement with this conclusion.[31]

Further inspection of Table 2 shows that $J_{3,4}$, whilst not absolutely constant, is always nearly equal to $J_{1,2}$.   This implies that the ring is symmetrically deformed out of the plane, and the fact that $J_{2,3}$ is very small determines the precise mode of puckering.   These coupling constants can arise only if the centres $C_{(2)}$ and $C_{(3)}$ are displaced below and above the plane containing the other ring members, *i.e.*, the furanose ring in every one of the molecules studied appears to exist in solution in a " skew " conformation in which atoms $C_{(2)}$ and $C_{(3)}$ are displaced in opposite senses from the plane of the other ring-atoms (Fig. 3a).

FIG. 3.   (a) The conformation of the furanose ring in solution.   (b) The conformation of the 3,6-anhydro-derivatives (XI) and (XII) in solution.

(a)   (b)
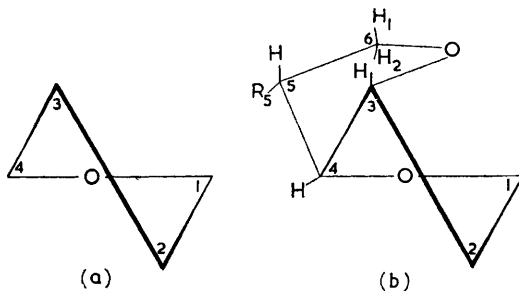
It is also possible to determine the conformation of the five-membered anhydro-ring in the two 3,6-anhydro-derivatives (XI) and (XII).   In each of these compounds $J_{3,4}$ and $J_{4,5}$ are approximately equal and are very different from $J_{5,6_1}$ and $J_{5,6_2}$.   This situation can arise only if the anhydro-ring is buckled so as to maintain a plane of symmetry through $C_{(4)}$ perpendicular to the $O-C_{(6)}$ bond, *i.e.*, this ring exists in an " envelope " conformation in which atom $C_{(4)}$ alone is displaced from the plane containing the other four ring-atoms. It is of considerable interest that these two compounds, (XI) and (XII), contain at one time both of the symmetric conformations available to five-membered ring compounds.

This purely qualitative discussion does not yield the sense in which $C_{(4)}$ is displaced from the plane of the other atoms which constitute the anhydro-ring.   However, this follows from the application of equation (1) to the system.

As mentioned above, the difficulty in using the equation is to know the parameters that are required.   Lenz and Heeschen [10] had some success in applying the equation to six-membered carbohydrate rings by multiplying both terms given by Karplus by a factor of 1·09.   There appears to be no theoretical justification for such a step and so in this case only the angular dependent term has been multiplied by this factor to give the following values for J_0 : 9·27 for $\phi \leqslant 0 \leqslant 90°$ and 10·36 for $\phi \leqslant 90 \leqslant 180°$.   It should be stressed that this is an entirely empirical approach which, however, can be tested since the anhydro-rings of compounds (XI) and (XII) each contain a $-CH_2-CH\langle$ grouping.

[29] Beckett, Freeman, and Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 4227;   Raphael and Trenlake, *Chem. and Ind.*, 1953, 1286.
[30] Ottar, *Acta Chem. Scand.*, 1947, **1**, 283.
[31] Hall, Hough, Pachler, and McLauchlan, unpublished results.

Thus, according to the sense in which $C_{(4)}$ is displaced from the plane of the other ring-atoms, the two dihedral angles calculated by applying the equation with the above parameters to $J_{5,6_1}$ and $J_{5,6_2}$ should either add or subtract to $120°$.

Taking the 5-hydroxy-3,6-anhydro-derivative (XII) as an example, and denoting the dihedral angle associated with $J_{5,6_1}$ by $\phi_{5,6_1}$, and similarly for $J_{5,6_2}$, we obtain two assignments according to whether we consider $J_{5,6_1}$ or $J_{5,6_2}$ to correspond to angles of less than or greater than $90°$:

$$(1) \quad \phi_{5,6_1} = 34°, \; \phi_{5,6_2} = 154° \, 6' \qquad (2) \quad \phi_{5,6_1} = 141° \, 42', \; \phi_{5,6_2} = 18°$$

Each of these assignments gives the difference in dihedral angles as nearly $120°$. This not only justifies the use of the equation but also defines the sense of the deformation in the anhydro-ring: $C_{(4)}$ moves out of the plane of the other four ring-atoms on the same side as the larger 5-substituent and the overall conformation of the molecule is as shown in Fig. 3b.

Since the anhydro-ring buckles in a known way, it is possible to calculate the dihedral angles around the ring as functions of the angle (θ), produced by the buckling, between the $O, C_{(3)}, C_{(6)}$ plane and the $C_{(3)}, C_{(4)}, C_{(5)}$ plane. The full calculation of the conformation of a five-membered ring compound is of considerable complexity but if it is assumed [11] that, on buckling, the bond lengths are unaltered and that two of the ring angles are equal but different from the other three (which are all equal), we obtain for $\theta = 50°$,

$$\phi_{3,4} = \phi_{4,5} = 49° \text{ and } \phi_{5,6} = 30° \text{ and } 150°$$

where $\phi_{3,4}$ and $\phi_{4,5}$ are defined to be the dihedral angles separating the C–H bonds at the two centres given. Application of equation (1), with the values of J_0 listed above to the observed coupling constants, gives

$$\phi_{3,4} = \phi_{4,5} = 47° \, 48'$$

This is in excellent agreement with the calculated value and indicates that assignment (1), above, which gave $\phi_{5,6_1} = 34°$, is correct besides constituting further justification for using these values of J_0. This also means that the $J_{5,6}$ coupling constant of 6·1 c./sec. corresponds to the smaller dihedral angle and assigns $H_{(6_1)}$ and $H_{(6_2)}$ which are as shown in Fig. 3b.

Experimental.—The samples of all thirteen 1,2-*O*-isopropylidene-α-D-*xylo*hexofuranose derivatives investigated were prepared by the methods given in their literature references.

The spectra were obtained in acetone solution on a Varian 60 Mc./sec. V.4200B spectrometer at approximately $25°$. Calibration was by the usual side-band technique, tetramethylsilane being used as internal reference. Since all the spectra are complex, it was sometimes necessary to run them in chloroform solution also and to make use of solvent-shift phenomena to observe parts of the spectra previously obscured.

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