Note

Conformation of methyl *O*-methyl-D-xylofuranosides: a p.m.r. study

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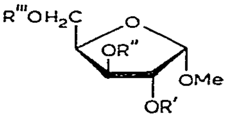
In contrast to six-membered ring systems, not much information has accumulated in the literature concerning the conformational analysis of five-membered ring systems. The difficulties encountered in such analysis are due to the very small energy differences between the various, possible conformations[1].

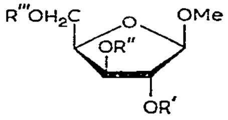
Abraham and McLauchlan[3] have calculated dihedral angles as a function of the puckering of the five-membered ring, and Hall[4] has investigated the conformation of some α-D-ribofuranose derivatives by p.m.r. spectroscopy. The conformations of a number of other pentofuranose derivatives, *e.g.* those of D-arabinose, D-xylose, D-ribose, and D-xylose, have also been investigated[5]. Coxon[6] studied the conformation of 1,2-*O*-benzylidene- and 1,2:3,5-di-*O*-benzylidene-α-D-glucofuranose and concluded that the furanoid ring in these compounds exists predominantly in a twist (*T*) conformation.

For most substituted furanoid sugars, as a result of steric and non-bonded interactions, some of the conformations of a certain segment of the pseudorotation cycle[2] are more heavily populated. We now report on the conformations of methyl *O*-methyl-D-xylofuranosides.

The chemical shifts (τ) of H-1–H-4, obtained from the first-order parts of the spectra, for seven anomeric pairs of methyl *O*-methyl-D-xylofuranosides are presented in Table I.



1 R′ = Me, R″ = R‴ = H
2 R′ = R‴ = H, R″ = Me
3 R′ = R″ = H, R‴ = Me
4 R′ = R″ = Me, R‴ = H
5 R′ = R‴ = Me, R″ = H
6 R′ = H, R″ = R‴ = Me
7 R′ = R″ = R‴ = Me



8 R′ = Me, R″ = R‴ = H
9 R′ = R‴ = H, R″ = Me
10 R′ = R″ = H, R‴ = Me
11 R′ = R″ = Me, R‴ = H
12 R′ = R‴ = Me, R″ = H
13 R′ = H, R″ = R‴ = Me
14 R′ = R″ = R‴ = Me

The anomeric proton for each methyl *O*-methyl-D-xylofuranoside appears as a well-resolved doublet. In cases where a methoxyl group is present at C-2, H-1 is

TABLE I

CHEMICAL SHIFTS (τ) OF THE XYLOFURANOSIDES **1–14**

Compound	*H-1*	*H-2*	*H-3*	*H-4*
1	4.91	5.97	5.20	5.58
2	4.92	5.46	5.79	5.35
3	4.80	5.22	5.29	5.44
4	4.89	5.99	5.77	5.44
5	4.83	5.96	5.25	5.52
6	4.97	5.58	5.93	5.42
7	4.94	6.10	5.89	5.47
8	4.91	5.91	5.40	
9	4.81	5.40	5.91	5.21
10	4.76	5.36	5.36	5.18
11	4.94	6.06	6.00	5.37
12	4.91	5.98	5.43	
13	4.78	5.41	5.97	5.22
14	4.99	6.10	6.13	5.47

more shielded in the β-anomer. Where there is a free hydroxyl group at C-2, H-1 is more shielded in the α-anomer. The diamagnetic, upfield (τ) shift can be seen for compounds where there is a proton attached to a carbon atom carrying a methoxyl group.

TABLE II

THE FIRST-ORDER COUPLING CONSTANTS (Hz) OF METHYL *O*-METHYL-D-XYLOFURANOSIDES

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$
1	4.3	6.2	7.0
2	4.4	5.5	6.8
3	4.3	4.6	6.2
4	4.1	5.7	6.5
5	4.4	5.5	6.5
6	4.5	4.7	6.2
7	4.2	5.4	6.7
8	1.8	1.9	
9	1.5	2.6	6.0
10	0.8	2.0	5.0
11	1.5	2.3	
12	1.5	2.1	
13	1.0	2.0	5.6
14	1.5	2.5	6.5

The determination of the conformation of the fourteen methyl *O*-methyl-D-xylofuranosides is based on the coupling constants (Table II) and the dihedral angles derived therefrom[7].

A five-membered ring can exist in both symmetrical [envelope (*E*) and twist (*T*)[8]] and non-symmetrical conformations. Only the symmetrical conformations are considered here; the nonsymmetrical forms are, in view of the limited accuracy of the n.m.r. method, not considered[2]. Of the twenty theoretically possible, symmetrical conformations, that which predominates is determined by the nature of the substituents and the non-bonded interactions. Thus, the p.m.r. parameters can be interpreted only in terms of a group of most-populated conformations that are closely related energetically.

TABLE III

DIHEDRAL ANGLES (FROM DREIDING MODELS) FOR METHYL *O*-METHYL-α-D-XYLOFURANOSIDES

Conformation	$\phi_{1,2}$	$\phi_{2,3}$	$\phi_{3,4}$
$^2T_1$	35°	155°	25°
^2V	25°	155°	20°
$^2T_3$	35°	155°	30°

Table III shows the dihedral angles for methyl *O*-methyl-α-D-xylofuranosides estimated from Dreiding models. Only the values closest to those estimated from coupling constants are presented. The irrelevant values for the remaining seventeen less-populated conformers are not included. Based on the observed coupling-constants, the following dihedral angles were derived for methyl *O*-methyl-α-D-xylofuranosides **1**–**7**: $\phi_{1,2} = 35$–$55°$; $\phi_{2,3} = 130$–$150°$; $\phi_{3,4} = 20$–$40°$. Comparing these values with the ones obtained from the models, the following most-probable conformations for methyl *O*-methyl-α-D-xylofuranosides are proposed: $^2T_1$, ^2V, $^2T_3$ (Fig. 1). In view of the rapid interconversion of the individual conformers, the n.m.r. method does not allow identification of any particular predominating conformer.

The dihedral angles for the β-anomers were estimated in a similar manner and compared with the values obtained from the models. The estimated angles $\phi_{1,2} =$

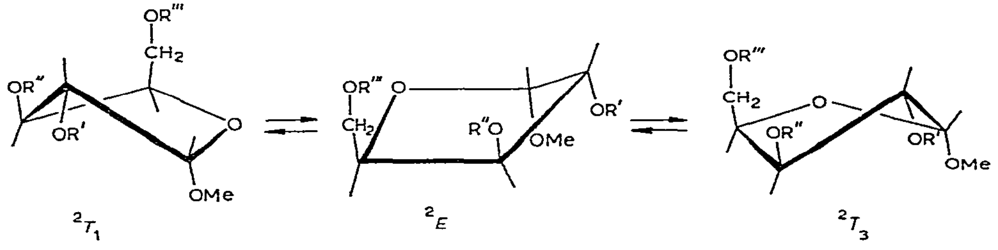


Fig. 1

100–120°; $\phi_{2,3} = 110–130°$; and $\phi_{3,4} = 30–50°$ are consistent with the following conformations: $^3T_2$, ^3V, $^3T_4$ (Fig. 2).

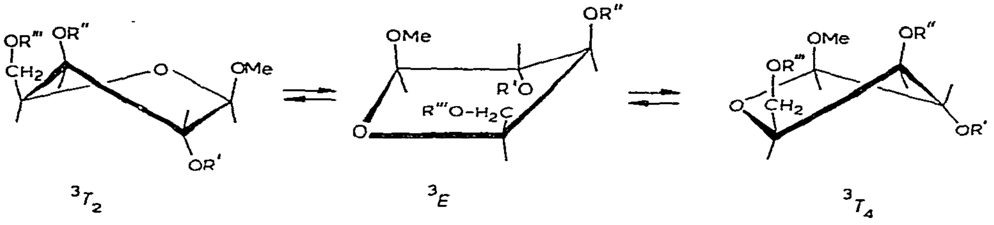


Fig. 2

The fact that there are different conformations for compounds in the α and β series shows the importance of the non-bonded interactions between O-1 and O-2, because the inversion of the configuration at the anomeric centre causes the variation in the population of the conformers. In order to clarify the influence of non-bonded interactions upon conformation, further study of model compounds is necessary.

EXPERIMENTAL

N.m.r. spectra were obtained for 10% solutions in pyridine at 25°, with an 80-MHz Tesla BS-487 B spectrometer. Better resolution was obtained in pyridine than in D_2O or $CDCl_3$. The proton-signal assignment was made by the INDOR technique. The methyl *O*-methyl-D-xylofuranosides (**1–14**) were synthesized according to published procedures[9–11].

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