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NOVEL UNEXPECTED EXAMPLES OF $^{5}J_{HH}$ LONG RANGE COUPLINGS IN CARBOHYDRATES.

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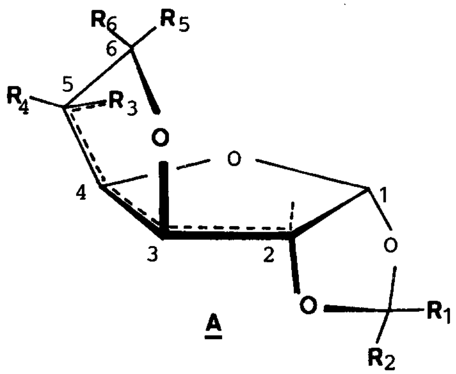
Summary: $^{5}J_{HH}$ Couplings proceeding through a H-C-C-C-C-H - fragment rather than a H-C-O-C-C-H - path in certain L-idofuranose derivatives are described. The probable mechanism is discussed.

In the course of our work towards the synthesis of a variety of specifically substituted carbohydrates of skeleton A[1] analysis of the NMR - spectrum of 1 was complicated by some ^{4}J and ^{5}J couplings within the ring protons, the $^{5}J_{H2,H5}$ coupling being the most striking one. During our literature search we found only two examples 13[2] and 14[3] of $^{5}J_{HH}$ couplings through five sigma bonds not interrupted by an heteroatom as in our case, whilst most of the shown examples involve H-C-O-C-C-H - fragments. Jochims in his excellent paper on NMR - analysis of a large group of similarily structured carbohydrates[4] did only mention couplings between H-1 and the endo methyl group of the isopropylidenering (e.g. R_2 in compound 4). As we could reproduce his findings but did notice some additional $^{4}J_{HH}$ couplings in our substances (which do not fall within the "virtual coupling limits"[5]) together with the above mentioned unexpected ^{5}J coupling, we decided to investigate the whole group of substances in more detail.

The results are summarized in table I.

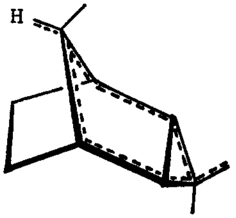
All observed spectra are in excellent agreement with simulated ones[6]. The sign of all $^{5}J_{HH}$ couplings (as determined by selective spin tickling[7] and taking the sign of vicinal couplings as positive) has been found to be positive in agreement with theoretical considerations[8] and most of the reported values in the literature (see e.g. ref. 4 and cited examples).



nr.	R_1	R_2	R_3	R_4	R_5	R_6
1	CH_3	CH_3	H	OBzl	OAc	H
2	Ph	H	H	OBzl	OAc	H
3	CH_3	CH_3	H	OH	=O	
4	CH_3	CH_3	OH	H	=O	
5	Ph	H	H	OH	=O	
6	Ph	H	OH	H	=O	
7	CH_3	CH_3	H	Br	=O	
8	CH_3	CH_3	Br	H	=O	
9	CH_3	CH_3	H	H	=O	
10	CH_3	CH_3	H	SetSH	=O	
11	CH_3	CH_3	OBz	H	OEt	OEt
12	CH_3	CH_3	H	F	=O	

Bzl = COPh , Bz = CH_2Ph

SetSH = SCH_2CH_2SH



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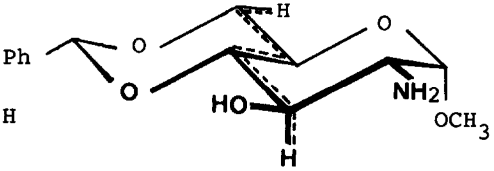

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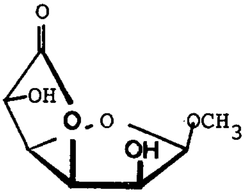

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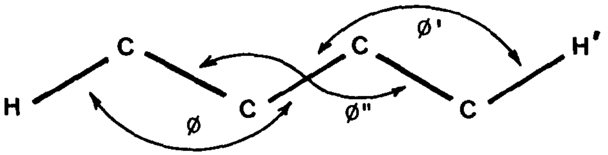
Table I. Coupling constants of some selected representatives of skeleton A (in Hz)

Nr.	Solvent	Temp. $({}^{o}K)$	${}^{5}J_{H2,H5}$	$J_{1,3}$	$J_{2,4}$	$J_{3,5}$	$J_{4,5}$	$J_{4,6}$	$J_{H1,PhCH}$
1	$CDCl_3$	301	0.8	0.3	0.4	0.3	0.4	0.4	-
2	$CDCl_3$	301	0.8	0.4	0.4	0.3	0.5		0.2
3	C_6D_6	377	0.9	0.5	0.5	0.5	0.6	-	-
4	C_6D_6	377	<0.1	<0.1	<0.1	<0.1	4.0	-	-
5	$Ac\text{-}d_6+D_2O$	301	0.8	0.5	0.5	0.4	0.6	-	0.1
6	$Ac\text{-}d_6+D_2O$	301	<0.1						
7	C_6D_6	301	1.0	0.5	0.4	0.4	0.5	-	-
8	C_6D_6	301	<0.1	0.5	0.5	<0.1	4.3	-	-
9	C_6D_6	301	H-5endo 0.95	0.4	0.4	0.5	0.5	-	-
			H-5exo <0.1	<0.1	<0.1	<0.1	4.5	-	-
10	C_6D_6	301	0.9	0.5	0.3	0.4	0.5	-	-
11	C_6D_6	301	<0.1						
15	$Ac\text{-}d_6+D_2O$	301	<0.1				6.2		

Compounds 1, 3 - 5 and 7 - 10 all show $J_{CH_3endo,H_2} = 0.15$ Hz, $J_{CH_3endo,H1} = 0.35$ Hz and $J_{CH_3endo,CH_3exo} = 0.65 - 0.7$ Hz.

As can be seen from table I only L-ido derivatives (H-5 endo) exhibit detectable $^5J_{H2,H5}$ couplings. Compound 9 proves that neither an oxygen nor any other substituent with lone pairs adjacent to H-5 is necessary for this type of coupling contrary to the findings of Jochims[4] for the other fragments of similarily structured carbohydrates investigated in his paper. With respect to these results it is interesting to notice, that in a fluoro-L-ido derivative (12, F-5 exo) Hall[9] found that the fluorine substituent exhibits detectable spin coupling with all ring protons exept H-2. Consequently some steric requirements have to be met in order to obtain $^5J_{H2,H5}$ couplings of appreciable size. In an attempt to rationalize such steric requirements for $^5J_{HH}$ couplings Barfield and Chakrabarti[10] describe equation (1)

$$^5J_{HH'} = (A\cos^2\phi + B\cos\phi + C) \times (A\cos^2\phi' + B\cos\phi' + C) \qquad (1)$$



regarding the central dihedral angle (Ø") as of no importance.

Force field calculations[11] as well as considerations of models did not reveal any substantial differences in the respective dihedral angles (Ø and Ø') for either one of these substances. The only differences are found in the shorter distances of H-2 to H-5 in L-ido-(1, 2, 3, 5, 7 and 10) against D - gluco-(4, 6 and 8) and D - manno-(15) derivatives. As neither the steric requirements for an extended W mechanism[12] nor the postulates of Jochims[4] are met in our case, it is more likely that the mechanism of this specific coupling proceeds through a direct way "through space" rather than an indirect one "through bonds"[10].

EXPERIMENTAL

NMR - spectra were taken in solvent and at temperature specified in table I on a Bruker WH 90 spectrometer. Choice was made according to maximum resolution and/or solubility. The synthesis of the substances is described elsewhere[1,13,14]. Calculations were performed on an Univac 1100/80 system equipped with a Benson plotter.

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