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^{1}H NMR Study of L-Fucopyranose and 2,6-Dideoxy-L-lyxo-hexopyranosides in D_2O

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The ^{1}H NMR parameters of α-, and β-L-fucopyranose and of 2,6-dideoxy-α- and -β-L-*lyxo*-hexopyranoses as well as their methyl pyranosides in D_2O have been determined at 300 MHz. The chemical shifts are compared to those of the corresponding D-galactopyranoses and 2-deoxy-D-*lyxo*-hexo-pyranoses.

Recently we have proposed shift increments in order to predict the chemical shifts of the ring protons in aldohexopyranoses relative to those of β-D-glucopyranose. We were able to refine and extend the increment values proposed by Lemieux.[1] Extensions were possible for methyl pyranosides,[2] aldopentopyranoses,[3] D-fructopyranose,[3] and disaccharides.[4] We have further correlated the shift data of the model compound with those in 2-deoxyaldohexopyranoses [5] and rhamnoses.[6] In the present study we report on the results obtained from a more general study of 2,6-dideoxy-aldohexopyranoses. The results were obtained from analysis of the spin systems observed at 300 MHz.

RESULTS AND DISCUSSION

The ^{1}H NMR parameters obtained from the 300 MHz spectra of α- and β-L-fucopyranose and of 2,6-dideoxy-α- and β-L-*lyxo*-hexopyranoses as well as of their methyl pyranosides are shown in Table 1.

The chemical shifts of the aldoses. In order to extrapolate the shift increments from aldohexopyranoses to 6-deoxy aldohexopyranoses it is necessary to introduce a set of corrections resulting from the substitution of CH_2OH (C-6) by CH_3. From a study of the chemical shifts of L-rhamnoses and D-mannoses,[6] this substitution was found to slightly influence H-1, -2, -3, and -5, but H-4 was shielded by −0.23 ppm in the deoxy sugar. Similar results are now observed when the chemical shifts of the ring protons of the fucopyranoses are compared to those of the corresponding anomers of the galactopyranoses, although for H-4 the upfield effect in the 6-deoxy sugar is found to be somewhat smaller (−0.18 ppm) and the downfield effect on H-5 somewhat larger (+0.09 to +0.11 ppm). Thus, when epimerizing an equatorial OH to an axial OH the vicinal axial H-5 undergoes a downfield shift of +0.37 to +0.40 ppm if geminal to a CH_3-group, and of +0.26 to +0.29 ppm [3] if it is geminal to a CH_2OH-group.

In order to evaluate the influence of the substitution of the CH_2OH by a CH_3 upon the chemical shifts of H-2, we have compared the chemical shifts of 2,6-dideoxy-L-*lyxo*-hexopyranose with those of 2-deoxy-L-*lyxo*-hexopyranose [6] (values between brackets in Table 1). An upfield shift is found for H-2_{ax} and H-2_{eq} of, respectively, −0.02 to −0.07 ppm and −0.03 to 0.04 ppm. It is noticeable that no shift difference is observed between H-2_{eq} in rhamnose and mannose, but a slight upfield shift of −0.03 to −0.05 ppm is seen for H-2_{ax} comparing fucose with galactose. We therefore propose a mean value of −0.03 ppm, as the correction for both protons in a 6-deoxy compound.

Table 1. ^{1}H NMR parameters of L-fucopyranose and 2,6-dideoxy-L-*lyxo*-hexopyranoses and their methyl glycosides.

Chemical shifts	H-1	H-2_{ax}	H-2_{eq}	H-3	H-4	H-5	CH_3-6	OMe
α-L-Fucopyranose[a]	5.20 (−0.07)	3.76 (−0.05)	—	3.86 (−0.02)	3.81 (−0.18)	4.20 (+0.11)	1.21	
β-L-Fucopyranose[a]	4.55 (−0.03)	3.45 (−0.03)	—	3.64 (−0.01)	3.75 (−0.18)	3.80 (+0.09)	1.25	—
2,6-Dideoxy-α-L-*lyxo*-hexopyranose[a]	5.35 (−0.05)	1.89 (−0.02)	1.81 (−0.03)	4.09 (−0.01)	3.69 (−0.18)	4.13 (+0.09)	1.21	—
2,6-Dideoxy-β-L-*lyxo*-hexopyranose[a]	4.81 (−0.06)	1.61 (−0.07)	1.98 (−0.04)	3.87 (+0.01)	3.59 (−0.19)	3.66 (+0.06)	1.25	—
Methyl 2,6-dideoxy-α-L-*lyxo*-hexo-pyranoside[a]	4.88 [−0.47]	1.89 [0]	1.83 [+0.02]	4.01 [−0.08]	3.68 [−0.01]	3.96 [−0.17]	1.23	3.35
Methyl 2,6-dideoxy-β-L-*lyxo*-hexo-pyranoside[a]	4.53 [−0.28]	1.59 [−0.02]	1.97 [−0.01]	3.88 [+0.01]	3.60 [+0.01]	3.66 [0]	1.27	3.52
Coupling constants	J(1,2ax)	J(1,2eq)	J(2eq,2ax)	J(2ax,3)	J(2eq,3)	J(3,4)	J(4,5)	J(5,CH_3-6)
α-L-Fucopyranose	3.9	—	—	10.0	—	3.4	~1.0	6.5
β-L-Fucopyranose	7.9	—	—	10.0	—	3.4	~1.0	6.5
2,6-Dideoxy-α-L-*lyxo*-hexopyranose[b]	3.2	1.9	−12.8	11.4	6.2	3.0	0.8	6.5
2,6-Dideoxy-β-L-*lyxo*-hexopyranose[b]	9.8	2.0	−12.2	12.0	4.6	3.4	0.8	6.5
Methyl 2,6-dideoxy-α-L-*lyxo*-hexopyranoside[b]	3.6	1.4	−13.2	11.3	6.6	3.2	0.8	6.6
Methyl 2,6-dideoxy-β-L-*lyxo*-hexopyranoside[b]	10.1	~2.0	−12.2	12.2	~5.0	~3.2	~1.0	6.5

[a] Values between brackets are the increment *vs.* the corresponding anomers of D-galactopyranose, and 2-deoxy-L-*lyxo*-hexopyranose, values between squared brackets are the increments *vs.* corresponding anomers of 2,6-dideoxy-L-*lyxo*-hexopyranoses. Positive values are used for deshielding. [b] Long range couplings are observed between (H=2_{eq}, 4_{eq}), (H-1, H-5) and (H-1, H-3).

The chemical shifts of the aldosides. When we compare the chemical shifts of the ring protons of D-galactopyranose with those of the corresponding anomers of methyl D-galactopyranosides, almost no changes are observed, except for H-5 in the α-form for which an upfield shift of −0.19 ppm is found. This effect of an axial glycosidic OMe group on the axial H-5 has been recognized in previous studies.[2,6] This trend therefore remains valid for 2-deoxy sugars.

The upfield shift of −0.08 ppm for H-3 in the α-form of 2,6-dideoxy-α-L-*lyxo*-hexopyranose is rather unexpected. An upfield shift of −0.26 ppm and −0.43 ppm in, respectively, the β-, and α-form for the glycosidic protons of methyl glycosides has previously been observed[2] for galactopyranosides. The chemical shifts of H-2 in both anomers of the methyl pyranosides of 2,6-dideoxy-L-*lyxo*-hexopyranose have remained unaffected, despite the observation of a "methylation shift" in methoxy cyclohexane *vs.* cyclohexanol.[7] We have previously pointed out[5] that increments are substrate-sensitive, *e.g.* that additional corrections might be necessary if dealing with changes in the skeleton of changes in substitution.

Therefore, if we want to apply the proposed increment rules for aldohexopyranoses[2] on 6-deoxy-aldohexopyranoses (*cf.* Ref. 6), the following corrections are proposed for the α-, as well as for the β-forms): −0.05 ppm for H-1, −0.20 ppm for H-4 and +0.03 or +0.13 ppm for H-5 depending on the equatorial or axial orientation of OH-4. The correction of H-2 is −0.03 ppm, irrespective of its axial or

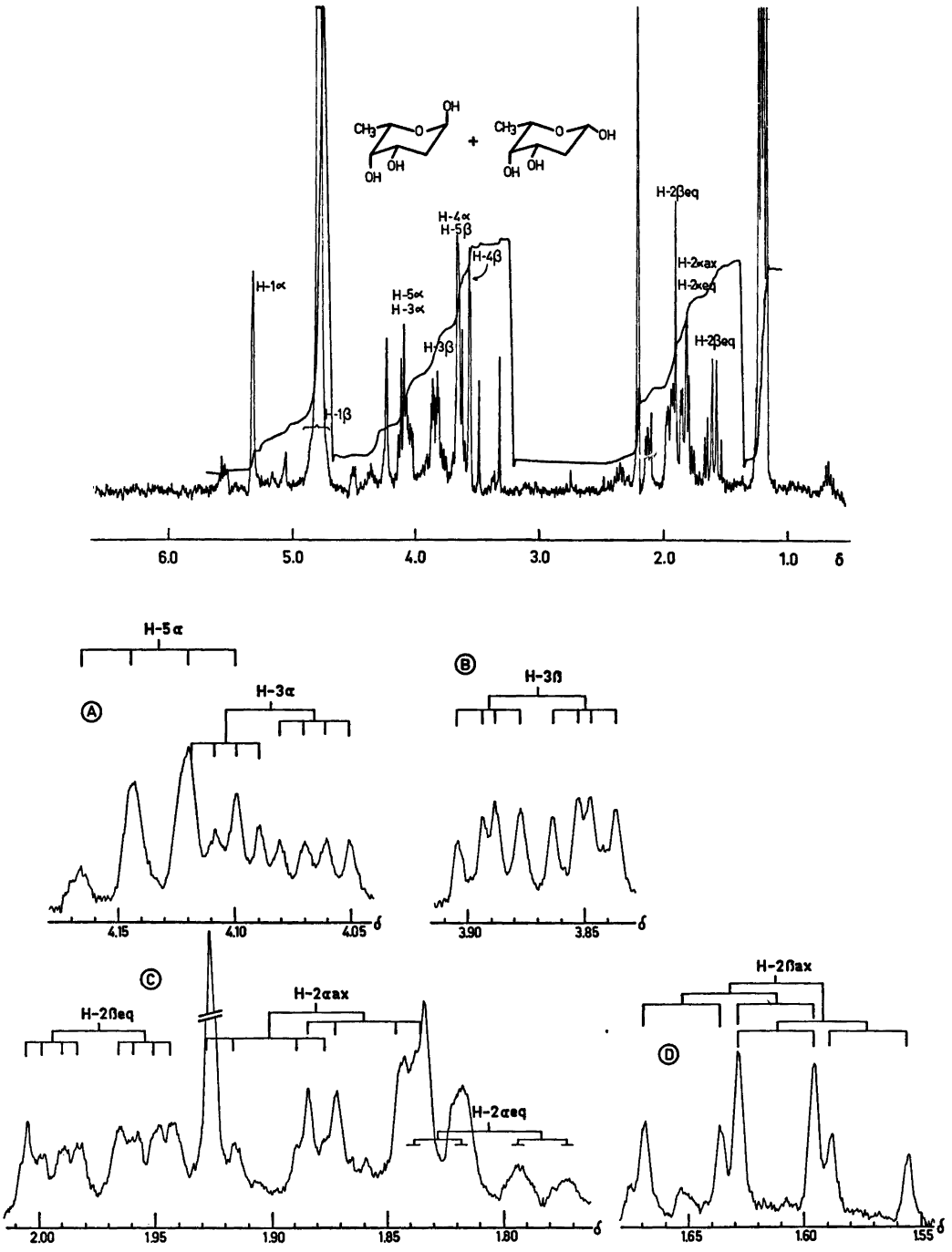

Fig. 1. ^{1}H NMR spectrum at 300 MHz in D_2O (DSS internal) of 2,6-dideoxy-L-*lyxo*-hexopyranoses (top) and extended regions (bottom). Both α- and β-pyranoses are present in appreciable amounts, but not the corresponding furanoses.

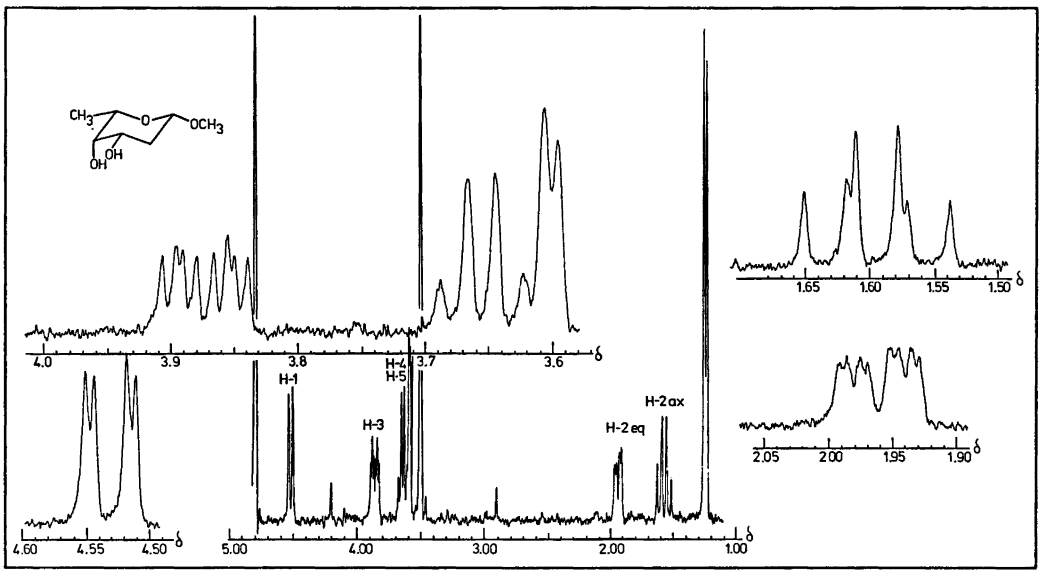

Fig. 2. ^{1}H NMR spectrum at 300 MHz in D_2O (DSS internal) of methyl 2,6-dideoxy-β-L-*lyxo*-hexopyranoside. Inserts are expanded regions.

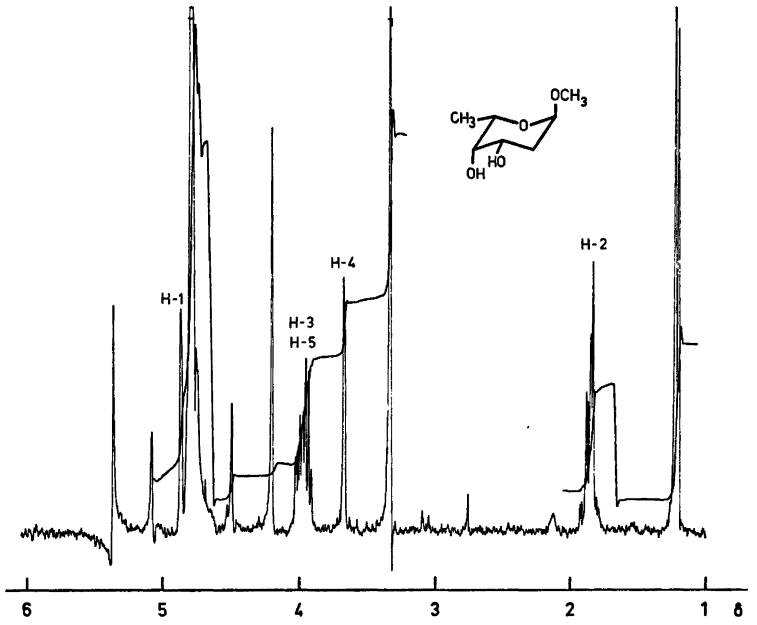

Fig. 3A. ^{1}H NMR spectrum at 300 MHz in D_2O (DSS internal) of methyl 2,6-dideoxy-α-L-*lyxo*-hexopyranoside.

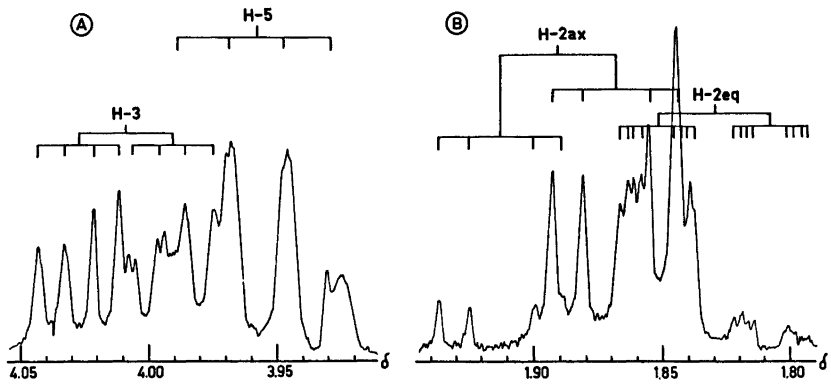

Fig. 3B. Extended regions of the spectrum given in Fig. 3A.

equatorial nature and irrespective of the geminal partner, H or OH.

EXPERIMENTAL

^{1}H NMR spectra were measured at 300 MHz and 19 °C with a VARIAN HR-300 spectrometer equipped with INDOR-facilities (SC 8525-2 unit). Concentrations were *ca.* 25 mg/ml D_2O with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (Sic) as the internal standard.

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