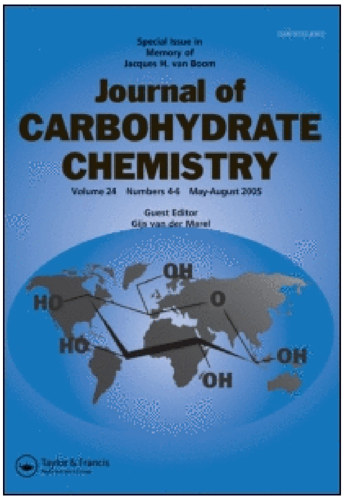

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^{13}C NMR Spectral Studies of Di- and Trideoxyaldohexoses

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^{13}C NMR SPECTRAL STUDIES OF DI- AND TRIDEOXYALDOHEXOSES

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ABSTRACT

^{13}C NMR spectral data of 3,6-dideoxy-, 3,4,6-trideoxyhexopyranoses and 3,6-dideoxyhexofuranoses , obtained from L-rhamnono-1,5-lactone are presented. Shifts induced on the ring carbons by C-1 acylation are analyzed for each pair of anomers.

INTRODUCTION

Di- and trideoxy sugars have been synthesized by diborane reduction of the corresponding deoxy aldonolactones, obtained *via* a β-elimination-stereoselective hydrogenation sequence developed in our laboratory.

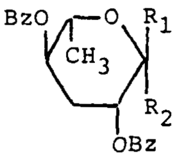
Starting from L-rhamnono-1,5-lactone, 2,4-di-O-benzoyl-3,6-dideoxy-L-arabino-hexopyranose (1);[1] 2,5-di-O-benzoyl-3,6-dideoxy-L-arabino-hexofuranose (2)[2] and 2-O-benzoyl-3,4,6-trideoxy-DL-threo-hexopyranose (3)[3] were obtained in good yields. ^{1}H NMR spectral studies suggested the presence of an anomeric mixture for the hexopyranoses and were consistent with the $^{1}C_{4}$ conformation for both anomers.[1,3] The hexofuranose 2, obtained exclusively as the α-anomer, is mainly in the $^{1}T_{O}$ conformation.[2]

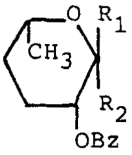
We now report on the ^{13}C NMR spectral studies of these compounds and their O-1 acyl derivatives, which confirm the structural and conformational assignments previously described.

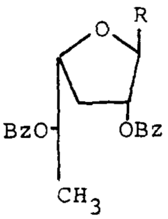
RESULTS AND DISCUSSION

^{13}C NMR spectra of acylated deoxyhexopyranoses and furanoses show five well-defined regions: a) Acyl carbonyl carbons appear at 164-170 p.p.m.; b) aromatic carbons at 127-134 p.p.m.; c) anomeric carbons at 90-105 p.p.m., with hexofuranose C-1 shifted downfield when compared with the isomeric pyranose;[4] d) O-acyl substituted ring carbons at 70-82 p.p.m., which were assigned by selective decoupling experiments and/ or by comparison with analogous compounds; e) deoxy carbons, at 16-32 p.p.m.. The regions of interest in our study were c, d and e, which comprise the aldose carbon atoms.

The ^{13}C NMR chemical shift assignments for 2,4-di-O-benzoyl-3,6-dideoxy-α- and β-L-arabino-hexopyranose (1α and 1β); 1,2,4-tri-O-benzoyl-3,6-dideoxy-α- and β-L-arabino-hexopyranose (4α and 4β); 2-O-benzoyl-3,4,6-trideoxy-α- and β-DL-threo-hexopyranose (3α and 3β); 1,2-di-O-benzoyl-3,4,6-trideoxy-α-DL-threo-hexopyranose (5); 2,5-di-O-benzoyl-3,6-dideoxy-α-L-arabino-hexofuranose







1 α R_1=OH; R_2=H
1 β R_1=H ; R_2=OH
4 α R_1=OBz; R_2=H
4 β R_1=H ; R_2=OBz

3 α R_1=OH; R_2=H
3 β R_1=H ; R_2=OH
5 R_1=OBz; R_2=H

2 R=OH
6 R=OAc

TABLE 1. ^{13}C NMR Chemical Shifts of Compounds 1-6 (δ p.p.m.)

Compound	C-1	C-2	C-3	C-4	C-5	C-6
1 α	90.9	71.2*	29.1	70.8*	66.8	18.0
1 β	94.4	74.1	32.7	70.5*	70.3*	18.3
4 α	90.5	70.0*	30.0	69.3*	69.4*	18.0
4 β	92.3	74.3	31.1	67.7	70.4	18.5
3 α	91.8	68.4	22.9	27.7	64.9	21.6
3 β	94.5	72.7	27.2*	27.3*	69.4	21.6
5	91.6	66.7	23.4	27.1	67.3	21.3
2	101.1	78.8	31.5	80.1	71.5	16.6
6	100.1	77.6	31.8	81.7	71.3	16.6

* The assignments may be interchanged

(2) and 1-O-acetyl-2,5-di-O-benzoyl-3,6-dideoxy-α-L-arabino-hexofuranose (6) are shown in Table 1.

If we compare the chemical shifts for compounds 1, 3 and 4, a downfield shift for carbons 1,2,3 and 5 is observed for the β-anomers. This result is in accord with the $^1C_4$ (L) conformation previously assigned to these compounds on the basis of ^1H NMR coupling constants.[1,3] Besides the expected downfield shift of C-2 due to the change of C-1 hydroxyl from an equatorial to an axial disposition, in the β-anomers there are additional CH interactions[5] between C-1, C-3 and C-5.

Benzoylation of C-1 induces an upfield shift for C-1 of 0.2-0.4 p.p.m. in the α series and 2.1 p.p.m. in the β series. The direction and relative magnitudes of these shifts are in agreement with those observed for L-rhamnose acetates.[6] This phenomenon seems to be a general one for pyranoses having an acyloxy group at C-1, and it has been suggested[6] that it may be caused by steric and through bond interactions between the p orbitals of the ring oxygen atom and the acyloxy group. In the β-anomers, the latter are more important and this fact is reflected in the greater chemical shift difference induced.

In the α series, the introduction of a C-1 benzoate causes an upfield shift (1.2-1.7 p.p.m.) in the β-carbon (C-2) and a significant downfield shift (2.4-2.6 p.p.m.) in C-5, whereas benzoylation of a β hydroxyl group has practically no effect on the shifts of C-2 and C-5. In the α-anomers, the characteristic effect upon the chemical shift of C-5 can be explained by 1,3-diaxial interaction, which would also account for the downfield shift observed for C-3 (0.5-0.9 p.p.m.)

The α-configuration assigned to the furanoid derivative 2,[2] on the basis of ^{1}H NMR data was confirmed by ^{13}C NMR spectroscopy. The anomeric carbon signal appears at 101.1 p.p.m. in accord with a trans-relationship between C-1 and C-2.[7] Acetylation induces an upfield shift on C-1 (1 p.p.m.) and C-2 (1.2 p.p.m.) as could be expected. The observed deshielding of C-4 (1.6 p.p.m.) can be explained by 1,3-interaction in the preferential $^{1}T_{O}$ conformation already established for compound 6 by DAERM analysis.[2] The deshielding of C-1 and C-4 in compound 2 when compared with compound 1 is characteristic of isomeric pyranoses and furanoses.[7]

It is interesting to compare the resonances for C-6, which appears in pyranoses at lower field than in furanoses, analogous to the resonances of 1,5-lactones compared with 1,4-lactones.[8] The downfield shift observed in the trideoxy derivatives 3 and 5 (3.3-3.6 p.p.m.) with respect to C-6 in the dideoxy compounds 1 and 4 can be explained by an additional 1,3-interaction between H-6 and H-4.

In our first description of compound 1 obtained *via* disiamylborane reduction of 2,4-di-*O*-benzoyl-3,6-dideoxy-L-*arabino*-hexono-1,5-lactone,[1] the complexity of the ^{1}H NMR spectrum didn't allow us to determine if we were observing one anomer or an anomeric mixture. ^{13}C NMR data showed signals for both anomers and the α,β-ratio (4.7:1) was calculated according to Horton and Walaszek.[9] A similar ratio was calculated for compound 4 (4.2:1), while in the trideoxy derivative 3, the preponderance of the α-anomer was lower (2.5:1).

^{13}C NMR spectroscopy proved to be a useful tool for the structural determination as well as an aid to corroborate the conformations of isomeric di- and trideoxy-aldoses.

EXPERIMENTAL

^{13}C NMR spectra were recorded in chloroform-*d* at 25.2 MHz on a Varian-XL-100 spectrometer using tetramethylsilane as internal standard. Signal assignments in compounds 1, 2 and 6 have been achieved from selective decoupling experiments.

Compounds 1, 2, 3, 4, 5, and 6 were synthesized as previously described[1-3].

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