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A. G. Ferrige^a; J. C. Lindon^a

^a Department of Physical Chemistry, Wellcome Research Laboratories, Kent, U.K.

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APPLICATION OF RESOLUTION ENHANCEMENT
IN FT NMR TO THE STRUCTURAL
DETERMINATION OF DEOXY SUGARS

Key words: NMR, digitoxose, canarose

A.G. Ferrige and J.C. Lindon

Department of Physical Chemistry

Wellcome Research Laboratories

Langley Court

Beckenham

Kent

U.K.

ABSTRACT

The ¹H NMR parameters of digitoxose and canarose, two 2,6-dideoxyhexopyranose sugars obtained from hydrolysis of cardio active glycosides, have been measured. The accurate coupling constants obtained through the use of resolution enhancement methods have been used to confirm the ring conformations.

INTRODUCTION

During the course of a study on glycosides extracted from Digitalis Lanata leaf we have had reason to examine the NMR

spectra of some of sugars formed as hydrolysis products. The sugars were known compounds but further confirmation of their structures was provided by their NMR spectra. This note presents the NMR data for two of the 2,6-dideoxyhexopyranoses for the first time. The NMR data for one of the other two possible structural isomers has already been published.¹

EXPERIMENTAL

¹H NMR spectra were measured on a Bruker HFX-90 spectrometer at 90 MHz in the pulse Fourier transform mode as solutions in dmsO-d₆. To improve the resolution in the frequency spectrum, the FID $f(t)$ was multiplied by a function of the form.

$$f'(t) = f(t) \cdot \exp (at - bt^2)$$

This function converts the normal exponential decay to that corresponding to a Gaussian lineshape after Fourier transformation. The parameter a is chosen to cancel the exponential decay of the resonance of interest and then b can be varied to produce the desired linewidth². The resolution obtained compared favourably with that measured at 300 MHz for similar sugars¹.

Any ambiguities in the assignment were removed by spin decoupling.

RESULTS

The full ¹H spectrum of one of the sugars, D-canarose (I), is shown in the figure. The sample consisted of a

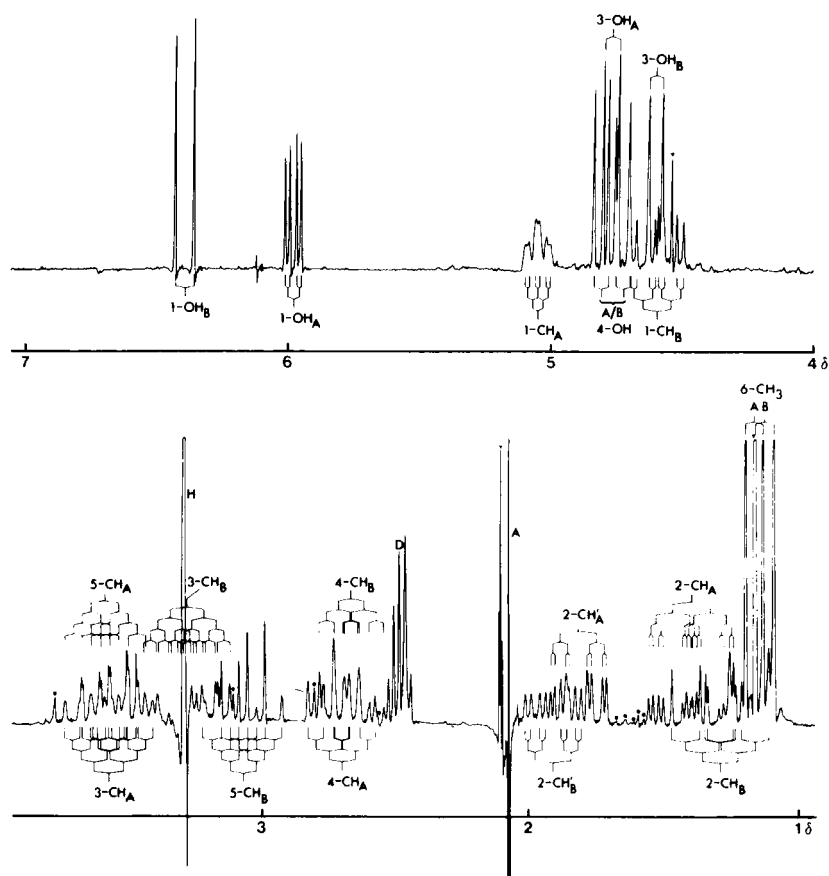
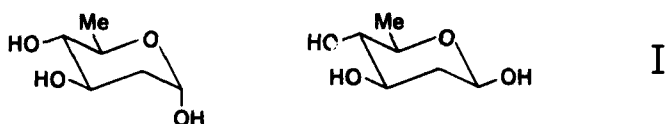


FIG. 1

90 MHz ^1H FT NMR spectrum of a 1:1 anomeric mixture of canarose in $\text{dmsO}-d_6$ at 24°C . The chemical shifts of the resonances are given in Table 1. Assignments are as shown on the figure. Major solvent impurities are marked as H = HOD, D = $\text{DmsO}-d_5$ and A = acetone. Peaks marked • are spinning sidebands and those marked ▼ are unidentified impurities.

Anomer A = α ; Anomer B = β

1:1 anomeric mixture which accounts for the complexity of the spectrum. However, most of the resonances could be assigned straightforwardly by pairing the coupling constants and hence the arrangement of the molecular fragments deduced.



Although the assignments of most of the resonances could be made on this basis some ambiguities remained and spin decoupling was necessary.

A strong irradiation at a position close to the chemical shift of one 3 proton and one 5 proton to low field of the H_2O resonance collapsed a coupling of 5.2 Hz on the H_2 - α equatorial proton showing that this 3 proton was from the α anomer. The same irradiation also effected the appearance of the resonances arising from the 4 protons and only one assignment of the nuclei gave a simulation in agreement with the observed spectrum. This experiment showed that the irradiation point was H_5 - α and that the H_4 - β proton is to higher field of H_4 - α . Furthermore the methyl resonances were unambiguously assigned.

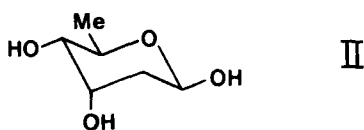
Further confirmation of the assignment of the α -anomer was provided by the long range 4-bond coupling $\text{HO}-\text{C}_1-\text{H}_{\text{ax}}$ of 1.4 Hz. The type of coupling can only appear

when all four intervening bonds form a planar W path and this is only possible when the OH is in an axial configuration.

The configuration evaluated above confirms the structure of the sugar as canarose, first discovered in 1963.³

We have also examined the NMR spectrum of β -D-digitoxose under similar conditions and the NMR parameters are included in Table 1 for comparison.

In addition to identifying the sugars, the coupling constants given in the Table also serve to confirm the conformations of the different anomers of canarose to be those given above (I). Similarly, β -D-digitoxose is shown to have the form (II).



These results follow from application of the predictive scheme for couplings in carbohydrates given by Anteunis and co-workers.^{1,4-6}

The configuration evaluated here confirms the structure of canarose which was first discovered as a hydrolysis product of a glycoside from *Digitalis canariensis*³ and later synthesised.⁷ It is also known as a constituent of glycosides from other sources, e.g. *Isoplexis isabelliana*.⁸

TABLE 1

Chemical shifts (ppm) and spin coupling constants (Hz) from the ^1H n.m.r. spectrum of α -canarose, β -canarose and β -digitoxose.

	CANAROSE		DIGITOXOSE
	α	β	β
$\delta(\text{H}_1)$	5.05	4.59	4.88
$\delta(\text{H}_2)$ ax	1.38	1.27	1.44
$\delta(\text{H}_2)$ eq	1.81	1.93	1.81
$\delta(\text{H}_3)$	3.53	3.29	4.41
$\delta(\text{H}_4)$	2.72	2.68	2.96
$\delta(\text{H}_5)$	3.58	3.10	3.59
$\delta(\text{CH}_3)$	1.14	1.11	1.10
$\delta(1\text{-OH})$	5.98	6.39	6.20
$\delta(3\text{-OH})$	4.77	4.60	4.43
$\delta(4\text{-OH})$	4.81*	4.73*	4.45
J 1,2 ax	3.5	9.1	9.2
J 1,2 eq	1.3	1.9	2.5
J 2 ax, 2 eq	-12.0	-11.7	-13.4
J 2 ax, 3	11.0	11.0	12.7
J 2 eq, 3	5.5	4.8	3.4
J 3,4	8.7	8.0	3.0
J 4,5	8.6	8.5	9.4
J 5, CH_3	5.9	5.8	6.2
J 1, 1-OH	3.6	6.2	6.5
J 1-OH, 2ax	1.4	0.0	0.0
J 3, 3-OH	5.0	4.3	3.0
J 4, 4-OH	4.8	4.7	6.6

* Assignments may be reversed.

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