The Proton Magnetic Resonance Spectra of Some Anomeric Glycopyranosides

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The α- and β-anomers of glycopyranoses and their derivatives, such as acetates and glycosides, are generally identified on the basis of Hudson's rule of isorotation[1] as well as by infrared absorption spectroscopy[2]. In the latter method, however, there are some difficulties; for example, α-lactose and its acetate can not be distinguished from the corresponding β-anomers[3].

Recently, Lemieux and his co-workers[4] have employed high resolution proton magnetic resonance (NMR) spectroscopy (40 Mc.) for the identification of the anomers of fully-acetylated glycopyranoses and have found that the doublet signals characteristic of the anomeric hydrogens in the equatorial and axial orientaions generally appear around 1.2 and 1.7 p.p.m. (from the chloroform peak) with a splitting of ca. 3 and 8 c. p. s., respectively. However, this method has not yet been used to identify the anomers of other important derivatives, particularly simple alkyl glycosides.

In the present investigation, the NMR spectra in chloroform of some anomeric acetylated glycopyranosides as well as of acetylated lactoses and maltose were measured at room temperature at 60 Mc. and the signals for the anomeric hydrogens were observed. The spectra are shown in Fig. 1, along with those of some acetylglycopyranoses for the sake of comparison.

As far as the spectra of pentaacetyl-β-glycopyranoses (I and II) and the corresponding methyl tetraacetyl-β-glycopyranosides (V and VI) are concerned, it is to be noticed that a doublet signal at 1.65 p. p. m. in the former spectra, that of the anomeric axial hydrogen coupled with the adjacent axial hydrogen, is absent in the latter spectra. In the latter, however, a new doublet signal with a splitting of 6.3 or 7.8 c. p. s. appears at 2.93 p. p. m. This is to be assigned to the anomeric hydrogen in the glycosides. The position of the signal is not surprising, since it is well-known that the signals of the α-protons in etherified alcohols appear at a field higher by ca. 1$\sim$1.5 p. p. m. than those in the corresponding acetates[5] and this shift occurs regardless of the axial and equatorial orientation on a cyclohexane ring[6].

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3) Y. Tsuzuki and N. Mori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 992 (1956).
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5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, London (1959), p. 55.
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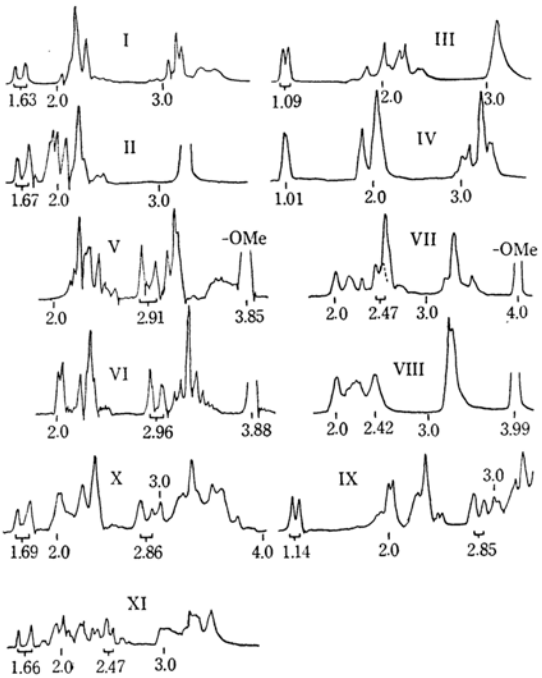

Fig. 1. NMR Spectra of acetylated sugars (in p. p. m. from $CHCl_3$).

Among the spectra of the corresponding α-anomers, a similar difference is observed. The spectrum of pentaacetyl-α-glucose (III) contains a doublet signal at 1.09 p. p. m. which is due to the anomeric equatorial hydrogen coupled with the adjacent axial hydrogen. In the spectrum of methyl tetraacetyl-α-glucoside (VII), the signal is absent, but a similar doublet signal with a splitting of 3 c. p. s. appears at 2.47 p. p. m., seemingly overlapping with a signal at 2.49 p. p. m. Similarly, with pentaacetyl-α-galactose (IV) a signal* which theoretically would be a doublet is present as a singlet at 1.01 p. p. m., while with methyl tetraacetyl-α-galactoside (VIII) a similar one appears at 2.42 p. p. m. Consequently, the signal at 2.45 p. p. m. in the α-glycosides, though not completely separated from other signals, seems to be that of the anomeric hydrogen.

In the spectra of the octaacetates of α- and β-lactose [4-*O*-β-D-galactopyranosyl-α- (IX) and -β-D-glucopyranose (X)], a doublet signal with a splitting of 6.3 or 7.4 c. p. s. appears at 2.86 p. p. m., in addition to the signal of the anomeric hydrogen in the α- or β-glucose unit. The former is of the anomeric axial hydrogen in the β-galactoside unit. In the case of the octaacetate of β-maltose (XI) [4-*O*-α-D-glucopyranosyl-β-D-glucopyranose], two characteristic signals are present, the one at 1.66 p. p. m. with a splitting of 6.7 c. p. s. being due to the anomeric hydrogen in the β-glucose unit and the other at 2.47 p. p. m. with a splitting of 3.5 c. p. s. due to that in the α-glucoside unit.

The above findings may be summarized as follows:

Pentaacetylglycopyranoses
α: 1.05 p. p. m. (J=3 c. p. s.)
β: 1.65 p. p. m. (J=7 c. p. s.)
Methyl tetraacetylglycopyranosides
α: 2.45 p. p. m. (J=3 c. p. s.)
β: 2.93 p. p. m. (J=7 c. p. s.)

Experimental

All compounds were prepared by the methods described in the literature cited; their melting points were as follows:

Pentaacetyl-D-glucopyranose[7], β(I) 131.5~132°C, α(III) 112~112.3°C

Pentaacetyl-D-galactopyranose[8], β(II) 143.5~143.7°C, α(IV) 96.5°C

Methyl tetraacetyl-D-glucopyranoside[7], β(V) 104~105°C, α(VII) 102°C

Methyl tetraacetyl-D-galactopyranoside[9], β(VI) 93~94.5°C, α(VIII) 86~87°C

Octaacetyllactose[10], β(X) 91~91.5°C, α(IX) 151.5°C

Octaacetylmaltose[11], β(XI) 162°C

All the spectra were measured in a 10~20% solution of the compound in chloroform using a Varian Model DP 60 NMR spectrometer equipped with a 60 Mc. r. f. unit. Tetramethylsilane was used in each case as an internal standard. Chemical shifts were obtained by the side-band method and are expressed in p. p. m. from chloroform to make them comparable with the data reported by Lemieux et al.[4]

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* Lemieux et al.[4] observed a singlet signal for the anomeric hydrogen in this compound.

7) C. S. Hudson and J. K. Dale, *J. Am. Chem. Soc.*, **37**, 1264 (1915).
8) C. H. Hudson and H. O. Parker, ibid., **37**, 1589 (1915); C. H. Hudson and J. M. Johnson, ibid., **38**, 1223 (1916).
9) J. K. Dale and C. S. Hudson, ibid., **52**, 2534 (1930).
10) C. S. Hudson and J. M. Johnson, ibid., **37**, 1270 (1915).
11) C. S. Hudson and J. M. Johnson, ibid., **37**, 1276 (1915).