Carbohydrate Research, 48 (1976) 125–127

Note

^{1}H-n.m.r. spectrum of methyl 2,3-anhydro-4,6-*O*-*p*-bromobenzylidene-α-D-mannopyranoside

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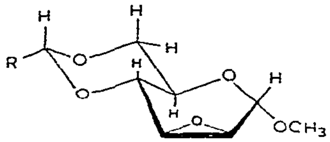
(Received December 1st, 1975; accepted for publication, December 5th, 1975)

In 1965, Buss *et al.*[1] published ^{1}H-n.m.r. data for several 2,3-epoxy, -episulphide, and -epimine derivatives of pyranosides. For methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (**1**), the signal at δ 4.25 was assigned to H-4, and a $J_{4,5}$ value of 5 Hz was reported. Essentially the same assignment for H-4 appeared in later papers[2,3].

The value of 5 Hz (Horton *et al.*[3] reported 6 Hz) for $J_{4,5}$ indicated either a small torsional angle between H-4 and H-5 and consequently an unusual conformation of the pyranoid ring in **1**, or a large deviation from the Karplus dependence[4]. X-Ray analysis[5] proved that the pyranoid ring in **1** has a typical half-chair conformation, seemingly leaving the second possibility.



1 R = C_6H_5
2 R = *p*-C_6H_4Br

Examination of the 100-MHz ^{1}H-n.m.r. spectrum (Fig. 1A) of methyl 2,3-anhydro-4,6-*O*-*p*-bromobenzylidene-α-D-mannopyranoside (**2**), which was identical (except for the aromatic protons) with that[2] of **1**, showed the three protons at δ 3.80–3.56 to be strongly coupled. Therefore the splitting of the signal at δ 4.25 does not necessarily correspond to the coupling constant. This view was confirmed by the spectrum for a solution of **2** in C_6D_6 (Fig. 1B), in which the signal in question appeared as a pair of doublets, indicating that not only was the previously reported value for $J_{4,5}$ incorrect, but also that the assignment of protons should be changed.

In the 360-MHz spectrum of a solution of **2** in C_6D_6, all of the signals could be assigned unequivocally, as shown in Fig. 1C. The values of the coupling constants

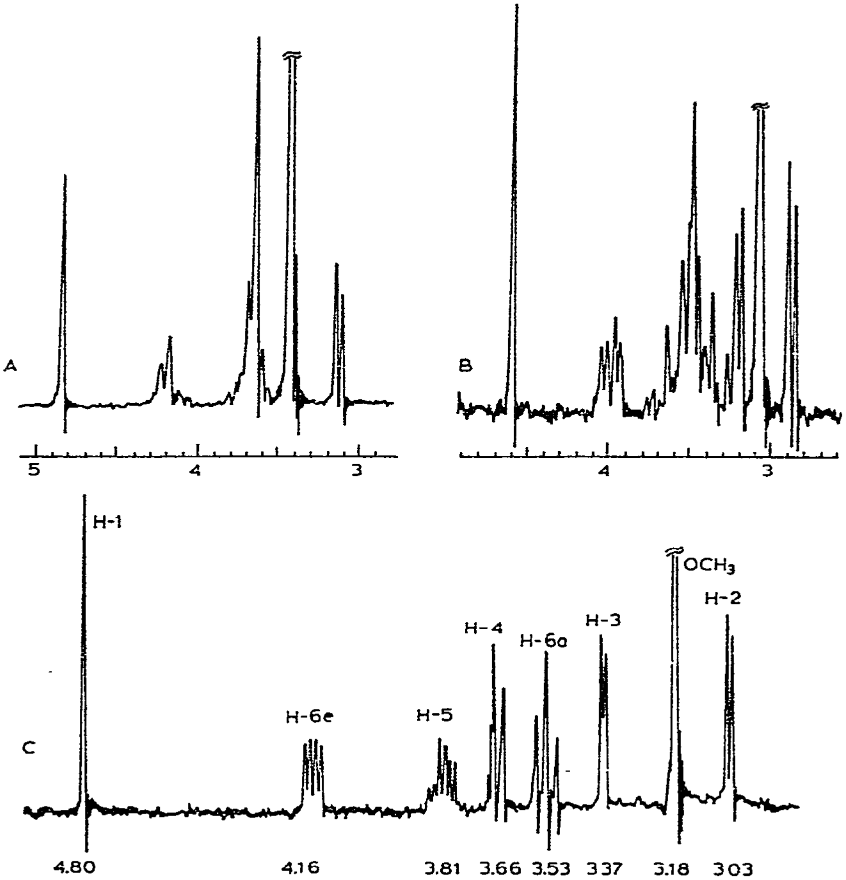


Fig. 1. Partial ^{1}H-n.m.r. spectra of methyl 2,3-anhydro-4,6-*O*-*p*-bromobenzylidene-α-D-mannopyranoside: *A*, 100 MHz in CDCl$_3$; *B*, 100 MHz in C$_6$D$_6$; *C*, 360 MHz in C$_6$D$_6$.

($J_{1,2}$ ~0, $J_{2,3}$ 3.6, $J_{3,4}$ ~0.5, $J_{4,5}$ 10.0, $J_{5,6a}$ 10.0, $J_{5,6e}$ 4.8, $J_{6a,6e}$ 10.2 Hz) for epoxide **2** are fully consistent with a $^{O}H_5$ conformation of **2** (and **1**) and conform to the Karplus-type dependence expected for pyranoid[6] and oxirane[7] ring protons.

ACKNOWLEDGMENT

The authors are grateful to Dr. H. P. Kellerhals of Bruker Spectrospin, 8017 Fällanden, Switzerland, for obtaining the 360-MHz spectrum.

EXPERIMENTAL

Methyl 2,3-anhydro-4,6-*O*-*p*-bromobenzylidene-α-D-mannopyranoside (**2**), m.p. 175–177°, was obtained, according to the procedure[8] described for **1**, from methyl α-D-glucopyranoside and *p*-bromobenzaldehyde *via* methyl 4,6-*O*-*p*-bromobenzylidene-α-D-glucopyranoside, m.p. 204–206°, and its 2-*O*-toluene-*p*-sulphonyl derivative, m.p. 196–197°. All compounds gave satisfactory elemental analyses and the expected i.r. and n.m.r. spectra.

^{1}H-n.m.r. spectra were recorded on Jeol JNM-4H-100 (at 100 MHz) and Bruker (at 360 MHz) instruments.

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