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CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF CARBOHYDRATE OXIRANE DERIVATIVES

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ABSTRACT

The ^{13}C-chemical shifts and $^{1}J_{C,H}$ values of two series of carbohydrate oxirane derivatives, namely methyl 2,3-anhydro-ribo- and -lyxofuranosides and methyl 2,3-anhydro-4,6-*O*-benzylidene-manno- and -allopyranosides have been determined. The assignment of ^{13}C resonances has been established mainly by the examination of the proton-coupled and the selective proton-decoupled spectra. The effect of the oxirane rings on the chemical shifts of β and γ carbon atoms (from the oxirane ring oxygen atom) has been observed. Large $^{1}J_{C,H}$ values associated with *cis* C–H bonds adjacent to the oxirane rings relative to those of *trans* counterparts have been found.

INTRODUCTION

Carbohydrate oxiranes are important reactive intermediates in the synthesis of a variety of modified sugars[1]. Their conformation and configuration have received considerable attention, especially in connection with the interesting stereochemistry of their reactions. ^{1}H-N.m.r. studies on aldopyranose oxirane derivatives[2–5] indicate that they are in half-chair conformations, while only little is known about the conformations of aldofuranose oxirane derivatives[6,7]. Recently, ^{13}C-n.m.r. spectroscopy has been applied to the study of various oxirane-containing compounds, and has proven to be a very useful technique as a probe for stereochemical information, such as the conformational analysis of 1-substituted 2,3-epoxypropanes[8] and cycloheptene oxide[9]; substituent effects in simple epoxides[10,11] and polyepoxides[12]; and configurational effects in steroidal epoxides[13], epoxycholesterols[14], epoxyphospholanes[15], and epoxynorbornanes[16]. In the present paper, we report the ^{13}C-n.m.r. spectra of methyl 2,3-anhydropentofuranosides **1–4** and methyl 2,3-anhydro-4,6-*O*-benzylidenehexopyranosides **5–8***. Their chemical shifts and coupling constants

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*After this work had been completed, the ^{13}C-n.m.r. chemical shifts of α-D-pyranoside oxiranes **5** and **7** were reported[17]. However, the chemical shifts of the corresponding β anomers and of furanoside oxiranes were not included, and a systematic discussion of chemical shifts was not given; coupling constants were not reported at all. The assignments of the ^{13}C-chemical shifts of **5** and **7** were in agreement with those in the present work, except in the case of C-2 and C-3 in **7**.

($^1J_{C,H}$) are interpreted and their dependence on the conformation of the carbohydrate and the stereochemistry of the oxirane ring are discussed.

RESULTS AND DISCUSSION

The signal assignments were aided by the previous ^{13}C-n.m.r. spectral studies

TABLE I

^{13}C CHEMICAL-SHIFT DATA[a] FOR CARBOHYDRATE OXIRANE DERIVATIVES

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-OMe*	*C-7*[b]	*Aromatic*
1	101.5	53.7	55.6	76.6	59.6		54.6		
2	101.8	54.4	55.1	76.4	59.6		55.7		
3	101.1	55.1	56.0	78.5	61.5		55.3		
4	101.7	54.8	55.4	78.6	61.7		54.8		
5	96.0	49.8	52.9	73.8	61.5	68.3	55.1	101.3	137.3 (C substituted), 128.9, 128.0 (*p*, *o*), and 126.2 (*m*)
6	99.1	50.1	54.1	73.7	67.8	68.3	56.3	101.2	137.3 (C substituted), 128.9, 128.0 (*p*, *o*), and 126.1 (*m*)
7	94.6	49.9	52.7	76.8	59.9	67.8	54.9	101.3	137.5 (C substituted), 129.9, 128.0 (*p*, *o*), and 126.1 (*m*)
8	97.1	50.6	54.7	76.4	60.5	68.0	55.8	101.4	137.4 (C substituted), 128.9, 128.0 (*p*, *o*), and 126.1 (*m*)

[a] In p.p.m. downfield from internal Me_4Si signal, for solutions in dimethyl sulfoxide-d_6. [b] Benzylidene-methine carbon.

TABLE II

ONE-BOND, ^{13}C–^{1}H, COUPLING-CONSTANT DATA[a] FOR CARBOHYDRATE OXIRANE DERIVATIVES

Compound	J_{C_1,H_1}	J_{C_2,H_2}	J_{C_3,H_3}	J_{C_4,H_4}	J_{C_5,H_5}	J_{C_6,H_6}	J_{OCH_3}	J_{C_7,H_7}[b]
1	169	193	193	146	142		145	
2	165	192	192	147	142		143	
3	168	194	192	148	141		141	
4	173	193	194	147	142		143	
5	169	184	182	153	148	145	143	161
6	163	184	184	153	148	149	144	165
7	161	186	182	145	152	154	143	162
8	171	188	183	141	149	148	144	165

[a] In Hz, for solutions in dimethyl sulfoxide-d_6. [b] Benzylidene-methine carbon.

of methyl pentofuranosides*,[18] and methyl 4,6-*O*-benzylidenehexopyranosides[19]. The ^{13}C-chemical shifts and the one-bond coupling constants are presented in Tables I and II, respectively. Complete analysis of the proton-coupled spectra was not attempted because the splitting patterns were second-order.

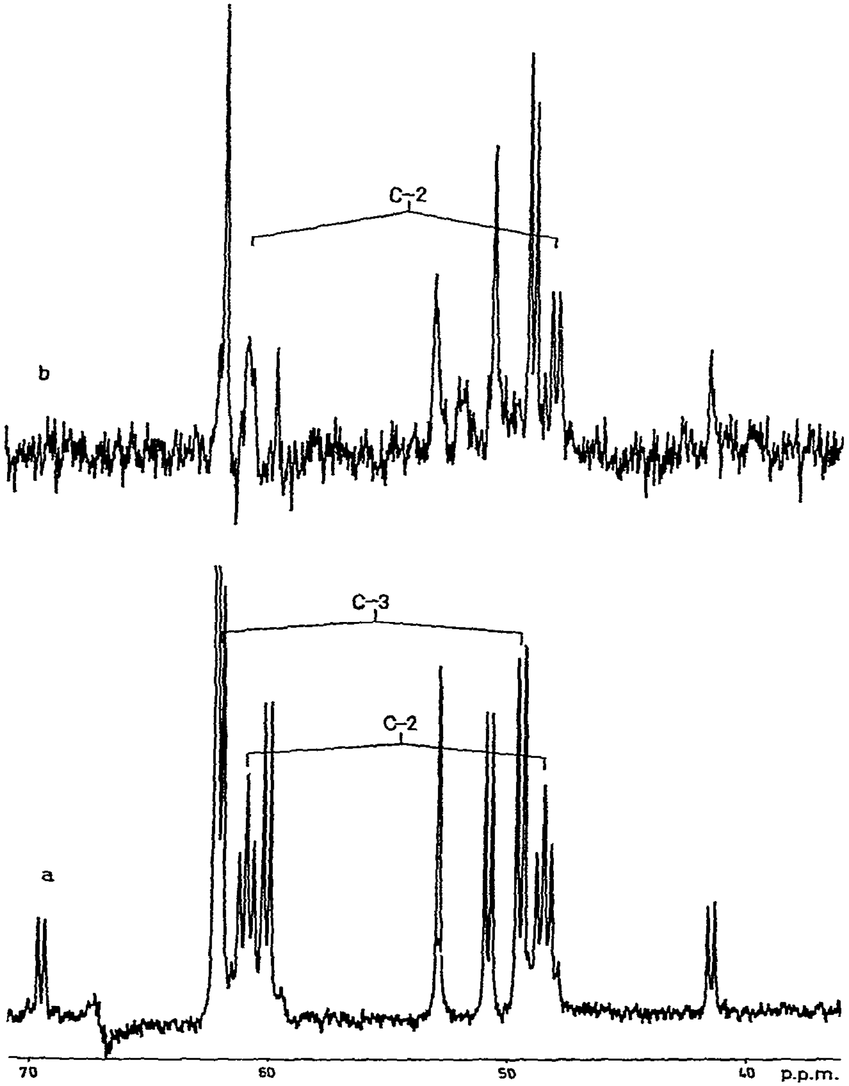

Fig. 1. Partial ^{13}C-n.m.r. spectrum of **4**: (a) proton coupled and (b) selective anomeric-proton decoupled.

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*In the present study, ^{13}C-n.m.r. spectra of methyl α- and β-D-lyxofuranosides and methyl α- and β-D-ribofuranosides in dimethyl sulfoxide-d_6 were recorded. No appreciable solvent-shifts were observed compared to the previous work[18].

In the spectra of methyl 2,3-anhydropentofuranosides **1–4**, the C-1, C-4, C-5, and the methoxy carbon signals were readily assigned by the examination of the proton-coupled and -decoupled spectra, and by the comparison of their chemical shifts with those of the corresponding parent methyl pentofuranosides. The distinction between C-2 and C-3 was achieved by the selective decoupling of the anomeric proton. Thus, the selective irradiation at the anomeric-proton resonance frequency resulted in a simplification of the C-2 signal into a doublet of doublets from a doublet of triplets, because of the loss of the long-range coupling with the anomeric proton, whereas the C-3 signal was unaffected (Fig. 1). However, in the case of **2**, it was difficult to distinguish between the C-2 and C-3 signals because of the complexity of the proton-coupled and the selective proton-decoupled spectra.

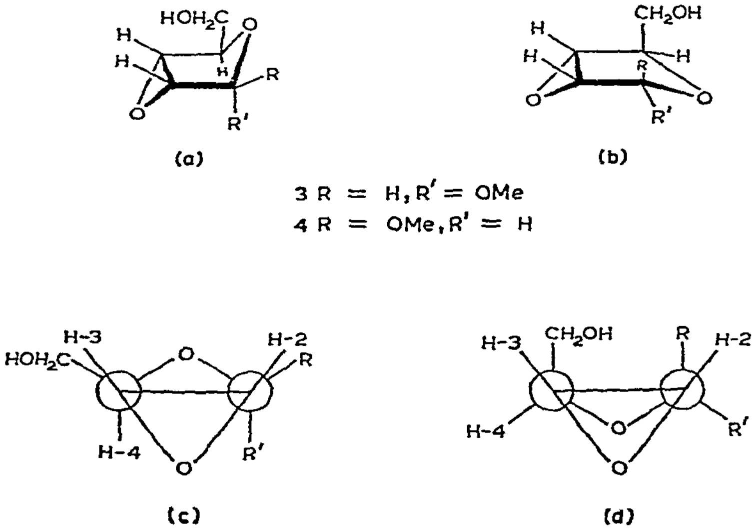
On the basis of the previous ^{13}C-n.m.r. studies on the derivatives of 4,6-*O*-benzylidenehexopyranosides[19–21], the aromatic carbon, the benzylidene-methine carbon, and the anomeric carbon signals in the spectra of oxiranes **5–8** were easily assigned. In the present study, the assignment of the anomeric carbon resonance was further substantiated by the selective decoupling of the anomeric proton. Inspection of the proton-coupled spectrum led us to identify the methoxyl carbon atom and C-6. Among the remaining unassigned resonances, the two oxirane-ring carbon atoms (C-2 and C-3) were distinguished by their high-field chemical shifts[22] and large $^1J_{C,H}$ coupling constants[23]. An unambiguous assignment to the C-2 and C-3 resonances in the spectra of **5–8** was readily made by the selective proton-decoupling technique. Carbon-4 and -5 signals were also easily assigned by the comparison of the spectra of **5–8** with those of the corresponding parent methyl 4,6-*O*-benzylidenehexopyranosides; these assignments were further substantiated by the $J_{C,H}$ coupling constants, as discussed later.

Inspection of the data recorded in Table I reveals that all of the anomeric carbons of furanoside oxiranes resonate at lower field than those of any pyranoside oxiranes. This difference provides a useful method for distinguishing between furanoside oxiranes and pyranoside oxiranes. Other parameters for distinguishing between furanoside oxiranes and pyranoside oxiranes are the one-bond coupling constants, $^1J_{C_2,H_2}$ and $^1J_{C_3,H_3}$. Those in furanoside oxiranes are appreciably larger than in pyranoside oxiranes. The difference may be attributed to the different ring sizes of the furanoside and pyranoside oxiranes. It has been well established[23] that the $^1J_{C,H}$ coupling constant of the five-membered ring is larger than that of the six-membered ring in the various monocyclic and polycyclic systems.

Chemical-shift data presented in Table I indicate that the orientation of the oxirane ring exerts a considerable effect on the chemical shifts of C-4 and C-5, of both the furanoside and pyranoside oxiranes. The C-4 signals in the spectra of riboside oxiranes **3** and **4** resonate at lower field than those of lyxoside oxiranes **1** and **2** by 1.9–2.2 p.p.m. This could partly be attributed to the *trans* relationship of the oxirane rings and the hydroxymethyl groups in **3** and **4**, whereas those in **1** and **2** are in a *cis* relationship. A similar effect is observed in the pyranoside oxiranes **5–8** as well. In mannoside oxiranes **5** and **6**, in which the oxirane rings are *cis* to axial

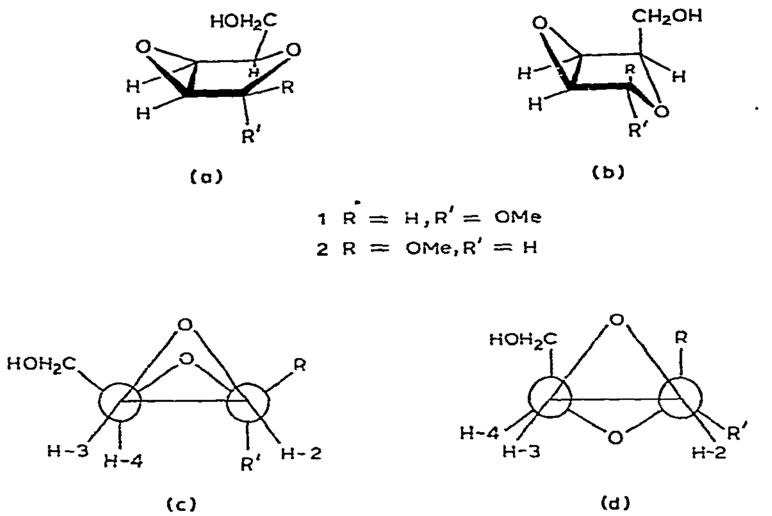
H-4 atoms, C-4 atoms are shielded by 2.7–3.0 p.p.m. with respect to those in alloside oxiranes **7** and **8**, in which the oxirane rings are disposed *trans* to the H-4 atoms. The chemical shifts of the C-5 atoms in furanoside oxiranes are also dependent upon the spatial relationship between the oxirane rings and the hydroxymethyl groups. In the case of a *cis* relationship, C-5 is shielded by 1.9–2.1 p.p.m. (compare data of **3** and **4** with those of **1** and **2**). This γ effect is also observed in the pyranoside oxiranes **5**–**8**. This result is consistent with that in a ^{13}C-n.m.r. study of cyclohexene oxide, in which Easton *et al.*[12] suggested that the shielding might be attributed to the spatial proximity of the γ-carbon atom to the lone-pair electrons of the oxirane-ring oxygen atom. However, Jefferies *et al.*[24] have suggested from the ^{1}H-n.m.r. study of diterpene epoxides that the long-range γ-shielding effects on proton chemical shifts might be attributed to the oxirane-ring current or the diamagnetic anisotropy of carbon–carbon and carbon–oxygen single bonds of the oxirane ring. Thus, the origin of the C-5 chemical-shift dependence on the spatial orientation of the oxirane ring is not clear, since the oxirane-ring current, the diamagnetic anisotropy, or simple steric effects may be operating.

According to the discussion in the preceding section, C-4 and C-5 chemical shifts in the ^{13}C-n.m.r. spectra of 2,3-anhydrofuranosides **1**–**4** may be employed in distinguishing between a *ribo* or a *lyxo* oxirane configuration. However, a distinction between anomeric pairs, namely α-D- and β-D-*ribo*, and α-D- and β-D-*lyxo* oxiranes, on the basis of C-1 and C-2 chemical shifts was not possible, as neither C-1 nor C-2 shieldings seemed to be sufficiently sensitive to the spatial orientation of the oxirane ring. This is in contrast to the observations in the methyl pentofuranoside series, where C-1 and C-2 shieldings clearly reflect the spatial relationship between substituents on them[25].



3 R = H, R' = OMe
4 R = OMe, R' = H

Scheme 1. Chair (a) and boat (b) conformations for **3** and **4** and their corresponding projection diagrams (c) and (d), respectively.



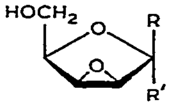
1 R = H, R' = OMe
2 R = OMe, R' = H

Scheme 2. Boat (a) and chair (b) conformations for **1** and **2** and their corresponding projection diagrams (c) and (d), respectively.

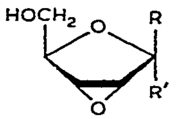
In order to explain the trends in chemical shifts in the ^{13}C-n.m.r. spectra of oxirane derivatives **1–4** rationally, an insight into the conformational behavior of these compounds is required. Thus, according to the study by Hall[6], oxiranes **3** and **4** may be regarded as existing in a chair conformation in which the bulky hydroxymethyl group is *quasi*-equatorially disposed. However, on the basis of molecular models (see Scheme 1), the boat conformation in the case of **3** cannot be completely disregarded. Hiraoka *et al.*[7] have suggested interconverting chair–boat conformations for ethyl 2,3-anhydro-5-*O*-(tetrahydro-2-pyranyl)pentofuranosides. On the basis of more recent spectroscopic and dipole moment studies by Creswell and Lafferty[26] and Malloy *et al.*[27] on 3,6-dioxabicyclo[3.1.0]hexane, and the examination of molecular models (see Scheme 2), oxiranes **1** and **2** could be regarded as existing solely in boat conformations at room temperature.

The aforementioned conformational considerations for oxiranes **1** and **2** suggest that the small upfield shift (0.3 p.p.m.) of C-1 in the spectrum of the α-D anomer **1** with respect to that in the spectrum of the β-D anomer **2** can be attributed to the operation of two counteracting shielding effects, namely, a γ-shielding effect due to 1,3-diaxial interaction between H-4 and the methoxyl group in the α-D anomer and shielding due to the *cis* relationship between the oxirane ring and the methoxyl group in the β-D anomer. However, the identical C-4 chemical shifts in the spectra of **1** and **2** still remain unexplainable on the basis of preferred boat conformations for **1** and **2**. Analogous conformational considerations for the ribofuranoside oxiranes **3** and **4** also failed to rationalise the essentially identical C-1 and C-4 chemical shifts in the spectra of the two epimers, thus raising doubts as to the preferred conformation of **3**.

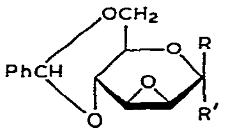
The half-chair conformations of methyl 4,6-*O*-benzylidenehexopyranoside



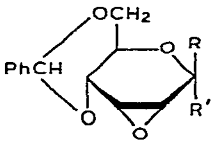
1 R = H, R' = OMe
2 R = OMe, R' = H



3 R = H, R' = OMe
4 R = OMe, R' = H



5 R = H, R' = OMe
6 R = OMe, R' = H



7 R = H, R' = OMe
8 R = OMe, R' = H

oxiranes have been well established from their ^{1}H-n.m.r. studies[4,5]. The rigid geometry of these compounds is clearly reflected by the C-1 and C-5 chemical shifts in the spectra for the anomeric pairs. Thus, in the spectra of the α-D anomers of the *manno* and the *allo* epoxides, the C-1 and C-5 signals are shifted upfield with respect to the corresponding signals in the spectra of the β-D anomers (see Table I). This upfield shift is attributed to the γ-steric compression shift, a phenomenon well known in six-membered cyclic compounds. It is interesting to note that, in the hypothetical configurational inversion **5**→**7**, C-1 experiences shielding (1.4 p.p.m.) as compared to deshielding (2.0 p.p.m.) associated with the transformation **8**→**6**. This is in violation to the earlier observations that a *cis* relationship of substituents on C-1 and C-2 is associated with shielding of C-1, as compared to the case when substituents are *trans* disposed. These trends in chemical shifts may be associated with some conformational distortion, for example ring flattening. Buss *et al.*[5] had observed that methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (**5**) and methyl 2,3-acetylepimino-4,6-*O*-benzylidene-2,3-dideoxy-α-D-mannopyranoside have smaller $J_{\mathrm{H-4,H-5}}$ values than the corresponding *allo* derivatives, and suggested that *manno* derivatives have somewhat flattened conformation.

The most interesting facet of the present investigation is the effect of the oxirane ring on $^{1}J_{\mathrm{C,H}}$ associated with the C–H bond adjacent to the oxirane ring. This is best exemplified by the $^{1}J_{\mathrm{C-4,H-4}}$ values of methyl 4,6-*O*-benzylidenehexopyranosides **5**–**8**. Thus, the $^{1}J_{\mathrm{C-4,H-4}}$ values of mannoside oxiranes **5** and **6** exceed the $^{1}J_{\mathrm{C-4,H-4}}$ values of the alloside oxiranes **7** and **8** by 10–12 Hz. This is attributed to the *cis* relationship between the axial H-4 atoms and the oxirane ring in **5** and **6**. A similar effect is also reflected in the $^{1}J_{\mathrm{C-1,H-1}}$ values in each of the pairs **5** and **7**, and **8** and **6**. In the case of pyranose sugars, it has been well established[28] that the anomer with an equatorial anomeric proton has a larger ($\sim$10 Hz) $^{1}J_{\mathrm{C-1,H-1}}$ value than the one with an axial anomeric proton. The larger $^{1}J_{\mathrm{C-1,H-1}}$ and $^{1}J_{\mathrm{C-4,H-4}}$ values in **5** and **6** may not be due to steric crowding[29], but rather due to the close proximity of the oxygen lone-pairs of electrons of the oxirane ring to the axial protons, thus facilitating lone-pair electron delocalization into the C–H bonds. Consideration of the $^1J_{C-1,H-1}$ values in **7** and **8** indicates that the effect of an oxirane function on the $^1J_{C,H}$ value associated with the adjacent C–H bond outweighs the effect of the sugar-ring oxygen atom, although minor factors such as steric effects might not be completely excluded.

In contrast to the discussion just presented, the $^1J_{C-4,H-4}$ values of furanoside oxiranes show no variation with respect to the oxirane-ring configuration. This may reflect that the $^1J_{C-4,H-4}$ value depends not only on the orientation of the oxirane ring but also on the rotamer population* of the hydroxymethyl group. For example, $^1J_{C-4,H-4}$ would have, in those cases in which the predominant rotamer has the C-4–H-4 and C-5–O-5 bonds eclipsed or nearly eclipsed, a value larger than the values for any other cases. In the eclipsed situation, the lone-pair electrons on the hydroxymethyl oxygen atom are in close proximity to the C-4–H-4 bond.

EXPERIMENTAL

Compounds. — Methyl 2,3-anhydro-α- (**1**) and -β-D-lyxofuranosides[30] (**2**) and methyl 2,3-anhydro-α- (**3**) and -β-D-ribofuranosides[31] (**4**) were prepared as reported by Baker *et al.* Methyl 2,3-anhydro-4,6-*O*-benzylidene-β-D-allopyranoside (**8**) was prepared by the method of Peat and Wiggins[32]. Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (**5**) and -α-D-allopyranoside (**7**) were prepared by standard procedures[33].

Methyl 2,3-anhydro-4,6-*O*-benzylidene-β-D-mannopyranoside (**6**) was obtained by alkaline hydrolysis of methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-β-D-glucopyranoside, which was prepared by selective tosylation[34] of methyl 4,6-*O*-benzylidene-β-D-glucopyranoside using phase-transfer catalysis. The tosyl derivative (2.05 g) was then dissolved in dry methanol (20 mL) containing sodium (0.16 g) and the mixture heated to reflux. Within 1 h, the product crystallized from the hot solvent. The crystals were collected from the cooled solution and washed with cold methanol (yield 1.10 g, 88%), m.p. 182–183° (lit.[32] m.p. 183°).

Spectrometry. — The ^{13}C-n.m.r. spectra were recorded with a Bruker HX-60 spectrometer equipped with an FT60M Fourier-transform accessory at 15.1 MHz, employing a ^{2}H-lock. Dimethyl sulfoxide-d_6 was the solvent, and tetramethylsilane the internal standard. Chemical shifts are given in p.p.m. downfield from Me_4Si. Sample concentrations were ~15% (w/v) in 10-mm (o.d.) sample tubes. For **6** and **7**, which have low solubility in $(CD_3)_2SO$, saturated solutions were used. The selective decoupling was accomplished by use of monochromatic irradiation at the resonance of the anomeric proton; the frequency was determined from ^{1}H-n.m.r. spectra obtained for the same sample as used for ^{13}C-n.m.r. spectra.

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*The rotamer population of the methoxyl group at the anomeric centre may also affect the $^1J_{C-1,H-1}$ value, but the effect should be much less pronounced.

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REFERENCES

1 For a review, see N. R. Williams, *Adv. Carbohyd. Chem. Biochem.*, 25 (1970) 109–179.
2 R. U. Lemieux, K. A. Watanabe, and A. A. Pavia, *Can. J. Chem.*, 47 (1969) 4413–4426.
3 J. G. Buchanan, R. Fletcher, K. Parry, and W. A. Thomas, *J. Chem. Soc.*, *B*, (1969) 377–385.
4 F. Sweet and R. K. Brown, *Can. J. Chem.*, 46 (1968) 1481–1486.
5 D. H. Buss, L. Hough, L. D. Hall, and J. F. Manville, *Tetrahedron*, 21 (1965) 69–74.
6 L. D. Hall, *Chem. Ind. (London)*, (1963) 950–951.
7 T. Hiraoka, T. Iwashige, and I. Iwai, *Chem. Pharm. Bull.*, 13 (1965) 285–291.
8 M. J. Shapiro, *J. Org. Chem.*, 42 (1977) 1434–1436.
9 K. L. Servis, E. A. Noe, N. R. Easton, Jr., and F. A. L. Anet, *J. Am. Chem. Soc.*, 96 (1974) 4185–4188.
10 D. R. Paulson, F. Y. N. Tang, G. F. Moran, A. S. Murray, B. P. Pelka, and E. M. Vasquez, *J. Org. Chem.*, 40 (1975) 184–186.
11 S. G. Davis and G. H. Whitham, *J. Chem. Soc. Perkin Trans. 2*, (1975) 861–863.
12 N. R. Easton, Jr., F. A. L. Anet, P. A. Burns, and C. S. Foote, *J. Am. Chem. Soc.*, 96 (1974) 3945–3948.
13 M. Sangare, B. Septe, G. Berenger, G. Lukacs, K. Tori, and T. Komeno, *Tetrahedron Lett.*, (1977) 699–702; K. Tori, T. Komeno, M. Sangare, B. Septe, B. Delpech, A. Ahond, and G. Lukacs, *ibid.*, (1974) 1157–1160.
14 W. G. Anderson, C. Y. Byon, M. Gut, and F. H. Bissett, *Tetrahedron Lett.*, (1976) 2193–2196.
15 C. Symmes, Jr., and L. D. Quinn, *Tetrahedron Lett.*, (1976) 1853–1856.
16 D. Zimmerman, J. Reisse, J. Coste, F. Plenat, and H. Christel, *Org. Magn. Reson.*, 6 (1974) 492–493.
17 A. S. Shashkov, A. Ya. Shmyrina, A. F. Sviridov, A. Kh. Arifkhodzhaev, and O. S. Chizhov, *Bioorg. Khim.*, 3 (1977) 1503–1511.
18 R. G. S. Ritchie, N. Cyr, B. Korsch, H. J. Koch, and A. S. Perlin, *Can. J. Chem.*, 53 (1975) 1424–1433; P. A. J. Gorin and M. Mazurek, *ibid.*, 53 (1975) 1212–1223; *Carbohydr. Res.*, 48 (1976) 171–186.
19 E. Conway, R. D. Guthrie, S. D. Gero, G. Lukacs, A. M. Sepulchre, E. W. Hagaman, and E. Wenkert, *Tetrahedron Lett.*, (1972) 4879–4882.
20 I. R. Burfitt, R. D. Guthrie, and R. W. Irvine, *Aust. J. Chem.*, 30 (1977) 1037–1043.
21 W. A. Szarek, D. M. Vyas, S. D. Gero, and G. Lukacs, *Can. J. Chem.*, 52 (1974) 3394–3400.
22 J. B. Stothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, 1972, pp. 270–271.
23 J. B. Stothers, ref. 22, pp. 332–348.
24 P. R. Jefferies, R. S. Rosich, and D. E. White, *Tetrahedron Lett.*, (1963) 1853–1855.
25 A. S. Perlin, *M.T.P. Int. Rev. Sci.: Org. Chem. Ser. Two, Carbohydr.*, 7 (1976) 13.
26 R. A. Creswell and W. J. Lafferty, *J. Mol. Spectrosc.*, 46 (1973) 371–380.
27 J. D. Lewis, J. Laane, and T. B. Malloy, Jr., *J. Chem. Phys.*, 61 (1974) 2342–2345; R. C. Lord and T. B. Malloy, Jr., *J. Mol. Spectrosc.*, 46 (1973) 358–370.
28 A. S. Perlin and B. Casu, *Tetrahedron Lett.*, (1969) 2921–2924; J. A. Schwarcz and A. S. Perlin, *Can. J. Chem.*, 50 (1972) 3667–3676; K. Bock, I. Lundt, and C. Pedersen, *Tetrahedron Lett.*, (1973) 1037–1040; K. Bock and C. Pedersen, *J. Chem. Soc. Perkin Trans. 2*, (1974) 293–297: G. K. Hamer and A. S. Perlin, *Carbohydr. Res.*, 49 (1976) 37–48.
29 A. S. Perlin, in E. Buncel and C. C. Lee (Eds.), *Isotopes in Organic Chemistry*, Vol. 3, Elsevier, Amsterdam, 1977, Chap. 4.
30 B. R. Baker, R. E. Schaub, and J. H. Williams, *J. Am. Chem. Soc.*, 77 (1955) 7–12.
31 C. D. Anderson, L. Goodman, and B. R. Baker, *J. Am. Chem. Soc.*, 80 (1958) 5247–5252.
32 S. Peat and L. F. Wiggins, *J. Chem. Soc.*, (1938) 1088–1097.
33 L. F. Wiggins, *Methods Carbohydr. Chem.*, 2 (1963) 188–191.
34 P. J. Garegg, T. Iversen, and S. Oscarson, *Carbohydr. Res.*, 53 (1977) c5–c7.