A ^{13}C Nuclear Magnetic Resonance Chemical Shift Study of *trans*-Fused Hexopyranoside Derivatives †

By **Eileen Conway** and **R. D. Guthrie**,‡ School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ
S. D. Gero,* **G. Lukacs**, and **A.-M. Sepulchre**, Institut de Chimie des Substances Naturelles, C.N.R.S., Gif-sur-Yvette, France

A detailed analysis of the ^{13}C n.m.r. spectra of methyl 4,6-*O*-benzylidene-D-glycopyranosides (and one ethylidene analogue) and their various C-2 and C-3 derivatives has led to complete assignment of chemical shifts. This study has enabled the effects of a variety of stereochemical features and a variety of functional groups (OH, OMe, O·COR, $O{\cdot}SO_2R$, NH_2, N_3) to be established.

THE first papers on ^{13}C n.m.r. of carbohydrates were published in 1969; since then studies on alditols,[1] inositols,[2] aldopyranoses,[3-9] methyl [3-6,10,11] and aryl [12] glycosides, glucobioses,[8,13] and oligosaccharides [8,9,13-16] have been described.

Several features of the spectra of such molecules have emerged: (i) the anomeric carbon signal generally occurs to low field because of its acetal nature; (ii) the signal due to C-6 of hexoses is situated at highest field, as this is a primary carbon atom; (iii) 1,3-diaxially disposed oxygen atoms have a shielding effect on the carbon nuclei involved, but this effect is the same or smaller than a similar oxygen–hydrogen interaction.

An investigation of the ^{13}C n.m.r. spectra of the more conformationally stable methyl 4,6-*O*-benzylidene-D-hexopyranosides (Table 1) and some of their derivatives has now been carried out, in the hope of establishing further stereochemical features of ^{13}C n.m.r. and their particular use in structural studies on carbohydrates.

The conformation of the pyranose ring in these systems has been shown by c.d. studies on cuprammonium complexes,[17] by ^1H n.m.r.[18] and i.r.[19] spectral studies, and by other methods [20] to be $^4C_1$(D). The variation of chemical shift with stereochemical change can therefore be studied with confidence. Empirical comparison of the diols, amino-alcohols, and deoxy-compounds in this series has led to the assignments shown in Table 1.

RESULTS AND DISCUSSION

Spectral Assignments.—The spectra of all the 4,6-*O*-benzylidene derivatives (1)—(13) and (15)—(23) show four peaks at low field due to the six aromatic carbon atoms. The positions of these signals vary only within experimental error throughout the whole series: 136·8 (quaternary carbon), 128·7 (*para*), 127·8, and 125·8 p.p.m.; the *ortho*- and *meta*-carbon atoms have not been assigned.

C-1 and C-7 (the acetal carbon atom linking the oxygen

† Preliminary communication, *Tetrahedron Letters*, 1972, 4879.
‡ *Present address:* School of Science, Griffith University, Nathan, Brisbane, Queensland 4109, Australia.

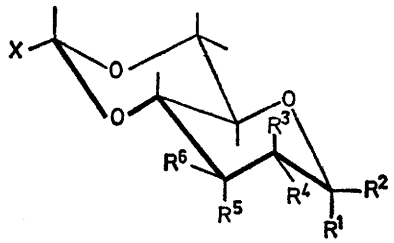
[1] W. Voelter, E. Breitmaier, G. Jung, T. Keller, and D. Hiss, *Angew. Chem. Internat. Edn.*, 1970, **9**, 803.
[2] D. E. Dorman, K. J. Angyal, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 1351.
[3] A. S. Perlin, B. Casu, and H. J. Koch, *Canad. J. Chem.*, 1970, **48**, 2596.
[4] D. E. Dorman and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 1355.
[5] L. D. Hall and L. F. Johnson, *Chem. Comm.*, 1969, 509.
[6] A. S. Perlin and B. Casu, *Tetrahedron Letters*, 1969, 2921.
[7] H. J. Koch and A. S. Perlin, *Carbohydrate Res.*, 1970, **15**, 403.
[8] A. Allerhand and D. Doddrell, *J. Amer. Chem. Soc.*, 1971, **93**, 2777.
[9] W. Voelter, E. Breitmaier, and G. Jung, *Angew. Chem. Internat. Edn.*, 1971, **10**, 935.
[10] B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, 1967, **89**, 5319.
[11] W. Voelter, E. Breitmaier, R. Price, and G. Jung, *Chimia (Switz.)*, 1971, **25**, 168.
[12] E. Breitmaier, W. Voelter, G. Jung, and C. Tänzer, *Chem. Ber.*, 1971, **104**, 1147.
[13] N. Yamaoka, T. Usui, K. Matsuda, K. Tuzimura, H. Sugiyama, and S. Seto, *Tetrahedron Letters*, 1971, 2047.
[14] W. W. Brinkely, D. Horton, N. S. Bhacca, and J. D. Wander, *Carbohydrate Res.*, 1972, **23**, 301.
[15] E. Breitmaier, G. Jung, and W. Voelter, *Chimia (Switz.)*, 1971, **25**, 362.
[16] J. B. Stothers, *Appl. Spectroscopy*, 1972, **26**, 1.
[17] S. T. K. Bukhari, R. D. Guthrie, A. I. Scott, and A. D. Wrixon, *Tetrahedron*, 1970, **26**, 3653.
[18] R. D. Guthrie and L. F. Johnson, *J. Chem. Soc.* (*C*), 1961, 4166; C. B. Barlow, E. O. Bishop, P. R. Carey, R. D. Guthrie, M. A. Jensen, and J. E. Lewis, *Tetrahedron*, 1968, **24**, 4517; C. B. Barlow, E. O. Bishop, P. R. Carey, and R. D. Guthrie, *Carbohydrate Res.*, 1969, **9**, 99; B. Coxon, *Tetrahedron*, 1965, **21**, 3481.
[19] H. Spedding, *Adv. Carbohydrate Chem.*, 1964, **19**, 23.
[20] C. B. Barlow and R. D. Guthrie, *J. Chem. Soc.* (*C*), 1967, 1194; *Carbohydrate Res.*, 1969, **11**, 53, 565; 1970, **13**, 199; R. D. Guthrie and A. M. Prior, *ibid.*, 1971, **18**, 373.

atoms on C-6 and C-4) are both bonded to two oxygen atoms, and would therefore be expected to give signals at lower field than the other carbon atoms, which are bonded only to one oxygen atom. These nuclei can be assigned the signals at *ca.* 100 p.p.m. Since the environment of C-7 is essentially unaltered throughout the series of compounds, the resonance at 101·4 ± 0·3 p.p.m. is attributed to this carbon atom. The methoxy-carbon signal can be assigned by comparison with previous data and occurs at relatively high field (55·5 ± 1·3 p.p.m.). Since the shielding of a particular nucleus varies with its orientation in the molecule, this carbon As expected, the C-6 signal varies little throughout the whole series and can be assigned as the peak at 68·4 ± 0·7 p.p.m. on the basis of comparison of all the members of the series. The spectrum of methyl 4,6-*O*-benzylidene [6,6′-$^2H_2$]α-D-glucoside confirmed the assignment of the C-6 signal in compound (4); its spectrum was identical with that of (4), except that the signal at 68·5 p.p.m. was missing.

Consideration of the C-1 anomeric pairs, the α- and β-*altro*- [(2) and (3)] and the α- and β-*gluco*-derivatives [(4) and (5)], in conjunction with the 2,3-dideoxy-derivative (7), leads to the assignment of the C-4 and

TABLE 1

^{13}C N.m.r. shifts (downfield from Me_4Si) of compounds (1)—(18)



X = Ph for all compounds except (14)[i](X = Me)

Compound	Hexose configuration	R¹	R²	R³	R⁴	R⁵	R⁶	C-1	C-2	C-3	C-4	C-5	C-6	C-7	OMe
(1)	α-*allo*	OMe	H	H	OH	OH	H	100·2	67·9	68·8	78·1	56·9	68·8	101·5	55·7
(2)	α-*altro*	OMe	H	OH	H	OH	H	101·6	69·6	68·8	76·0	57·8	68·8	101·8	55·0
(3)	β-*altro*	H	OMe	OH	H	OH	H	99·4	70·8 [a]	68·6 [a]	76·5	62·8	68·6	101·8	56·4
(4)	α-*gluco*	OMe	H	H	OH	H	OH	99·9	72·4	70·5	80·8	62·0	68·5	101·5	54·9
(5)	β-*gluco*	H	OMe	H	OH	H	OH	104·2	74·2	72·9	80·3	65·9	68·3	101·5	56·8
(6)	α-*manno*	OMe	H	OH	H	H	OH	101·7	70·6	68·0	78·5	62·9	68·4	101·7	54·4
(7)	2,3-dideoxy-α-*erythro*	OMe	H	H	H	H	H	98·1	29·0	23·5	77·9	64·5	69·1	101·6	54·2
(8)	3-deoxy-α-*ribo*	OMe	H	H	OH	H	H	98·9	67·0	32·6	76·1	63·4	68·9	101·3	54·6
(9)	3-deoxy-α-*arabino*	OMe	H	OH	H	H	H	100·5	67·4	31·4	73·5	64·6	68·9	101·8	54·3
(10)	α-*gluco*	OMe	H	H	OH	H	NH_2	99·4	72·1	52·4	81·0	62·2	68·7	101·5	55·0
(11)	α-*allo*	OMe	H	H	OH	NH_2	H	100·8	67·5	52·1	78·3	56·7	68·9	101·3	55·6
(12)	α-*altro*	OMe	H	OH	H	NH_2	H	101·6 [a]	69·4	52·0	75·9	57·6	68·8	101·8 [a]	54·8
(13)	α-*manno*	OMe	H	OH	H	H	NH_2	102·0	70·0	50·3	79·4	63·4	68·5	101·6	54·5
(14) [b]	β-*gluco*	H	OMe	H	OH	H	OH	104·1	74·2	72·9	79·8	65·9	67·7	99·4	56·7
(15) [d]	α-*allo*	OMe	H	H	OTs	OH	H	98·3	74·6	67·9	77·9	57·2	68·8	101·7	56·0
(16) [e]	α-*altro*	OMe	H	OTs	H	OTs	H	98·5	74·8 [a]	72·4 [a]	72·4 [a]	57·6	68·4	101·5	55·2
(17) [f]	α-*altro*	OMe	H	OH	H	NHMe	H	102·7	69·6	60·8	77·2 [c]	59·1	68·7	101·5	55·6
(18)	α-*altro*	OMe	H	OAc	H	N_3	H	98·5	70·2	58·3	75·7	57·5	68·5	101·9	55·3

[a] Values may be interchanged. [b] δ_{7-Me} 19·6 p.p.m. [c] Masked by chloroform signal. [d] δ_{Me} of tosyl, 21·1 p.p.m. [e] δ_{Me} of tosyl 21·0 p.p.m. [f] δ_{Me} of NHMe, 35·5 p.p.m.

atom should be more shielded in the α-anomer (*ax*) than in the β-anomer (*eq*). Thus the methoxy-carbon atoms in the anomeric *gluco* [(4) and (5)] and *altro* [(2) and (3)] pairs can be assigned. The Δ(β — α) values for these methoxy-carbon atoms are +1·9 and +1·4 p.p.m., respectively. Voelter *et al.* found Δ_{OMe}(β — α) for the methoxy-carbon atoms of various methyl gluco-pyranoside anomeric pairs to be +2·0 p.p.m.[9]

Owing to the β-effect of C-7, both C-6 and C-4 are strongly deshielded relative to the unsubstituted glycosides, in which the C-6 chemical shift is the next smallest after that of the methoxy-carbon atom. A comparison of methyl 4,6-*O*-benzylidene-β-D-glucoside (5) and methyl 4,6-*O*-ethylidene-β-D-glucoside (14) shows that the resonances of C-6 and C-4 are not affected by the anisotropic effect of the phenyl ring. C-5 signals. In compound (7) the unsubstituted methylene groups at C-2 and C-3 give rise to high-field signals, and since the signal at 69·1 p.p.m. is assigned to C-6, the remaining two signals must be due to C-4 and C-5. In the anomeric pairs, C-5 is β to C-1 and therefore experiences a 1,3-diaxial interaction with a C-1 oxygen atom *via* its own axial proton; hence it should be strongly shielded on changing from the β- to the α-anomer. C-4 is γ to C-1 and should not be affected much by changes at that centre. These considerations lead to the assignment of the C-4 and C-5 signals since, of the signals in each pair corresponding to the two signals in (7) assigned to C-4 or C-5, one is shifted upfield by 3·9 and 5·0 p.p.m. and the other is only slightly affected. Thus complete assignment of the spectrum of the dideoxy-compound (7) is possible. The

C-5 signal of all the compounds described was markedly upfield of its position in unsubstituted glycopyranoses and glycopyranosides.[3-11] While greater in magnitude in the present series, this shift is analogous to the observed effect of oxygens on C-2 and C-4 of aldohexopyranosides [3,6,7] and on the acetal carbon atom of 1,3-dioxans.[21]

The differences in chemical shifts of C-1 in (4) and (5), and in (2) and (3) [$\Delta_{C-1}(\beta - \alpha)$] are +4·3 and −2·2 p.p.m., respectively. The former value is in agreement with those found for free glycosides (+3·8 to +4·5 p.p.m.) when C-2 is equatorial.[3,4] However, in the latter pair the hydroxy-group on C-2 is axial and the overall deshielding on changing from the β(*eq*)- to the α(*ax*)-anomer is due to the predominance of the deshielding effect resulting from the removal of the *gauche* relationship between O-1 and O-2 over the shielding effect experienced as a result of acquiring an axial methoxy-group. This observation supports Perlin's findings of 0 p.p.m. (*lyxo*) and −0·6 p.p.m. (*manno*) for compounds with an axial hydroxy-group at C-2 and an equatorial one at C-3.[3] A comparison of the α-*gluco*-diol (4) and the 3-amino-α-*gluco*-derivative (10) leads to the assignment of the peak at 72·4 p.p.m. in the former to C-2, since in the latter C-3 is displaced to high field as a result of shielding by the amino-group; the remainder of the signals are relatively unaltered. All the signals of methyl 4,6-*O*-benzylidene-α-D-glucoside (4) and its 3-amino-derivative (10) can therefore be assigned. In the β-anomer (5), C-2 should be deshielded relative to compound (4) (since it is β to O-1) as should C-3 (which is γ to O-1), but on the basis of previous work the latter effect would be expected to be greater than the former or equal to it.[3] Thus the spectrum of compound (5) can be fully assigned.

Similar comparisons between the diols (1), (2), and (6) and the corresponding 3-amino-derivatives (11), (12), and (13), led to the complete assignment of all signals from these compounds and compounds (8), (9), and (14). Since the signal due to C-6 of the 3-amino-α-*altro*-derivative (12) could have been either of the two peaks at *ca.* 69 p.p.m., off-resonance decoupling was used to distinguish between them, since C-6 is coupled to two protons and C-2 to one proton. A similar confusion between C-3 and C-6 in the *manno*-diol (6) was resolved in an analogous way.

The spectrum of methyl 4,6-*O*-benzylidene-β-D-altroside (3) can be assigned by comparison with its α-anomer (2). On changing from the β(*eq*)- to the α(*ax*)-anomer, C-2 will experience shielding since it is β to O-1, and deshielding due to the removal of the *gauche* O-1/O-2 interaction. The overall shift [$\Delta_{C-2}(\alpha - \beta)$] should therefore be small. C-3 however, gains a 1,3-diaxial interaction with the axial oxygen atom *via* its own axial atom and a slight shielding would be expected. However, as both these effects are small, C-2 and C-3 are assigned as interchangeable. The ^{13}C n.m.r. spectrum of methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-β-D-altroside would resolve this problem.

Detailed Stereochemical Considerations.—(a) C-2 *Epimeric pairs* (*Table* 2). On changing from an equatorial to an axial substituent at C-2 a large shielding would be expected at C-4 which is γ to O-2. C-3 and C-1 should also be affected, but while C-1 will be consistently deshielded owing to the removal of a *gauche* O-2/O-1 effect (the series consists entirely of α-anomers), the effect at C-3 will vary depending on the orientation of the substituent. As can be seen, C-1 and C-4 show the expected shifts. C-6 is relatively unaffected, whereas C-5 is slightly deshielded. This latter effect was also observed by Perlin.[3] In the case of the 3-deoxy-derivatives (8) and (9), C-2 is deshielded by 0·4 p.p.m., implying that the loss of a *gauche* O-2/O-1 interaction has a greater effect than the acquiring of an axial hydroxy-group, and C-3, which is β to the axial hydroxy-group is shielded by 1·2 p.p.m.

TABLE 2

C-2 Epimers (α-anomers); a negative sign represents an upfield shift

	$\Delta\delta_C$	C-1	C-2	C-3	C-4	C-5	C-6
3-deoxy	(9)—(8)	+1·6	+0·4	−1·2	−2·6	+1·2	0
	(2)—(1)	+1·4	+1·7	0	−2·1	+0·9	0
ax C-3	(12)—(11)	+0·8	+1·9	−0·1	−2·4	+0·9	−0·1
	(6)—(4)	+1·8	−1·8	−2·5	−2·3	+0·9	−0·1
eq C-3	(13)—(10)	+2·6	−2·1	−2·1	−1·6	+1·2	−0·2

When the substituent on C-3 is axial, and the group on C-2 is changed from *eq* to *ax*, C-2 experiences the loss of two *gauche* interactions, O-2/O-3 and O-1/O-2 (deshielding), but gains an axial group (shielding); an overall deshielding is observed. C-3 loses a *gauche* O-3/O-2 interaction, but is β to the axial hydroxy-group. The resultant lack of shielding implies that the latter effect has approximately the same impact as the former. When the substituent at C-3 is equatorial, C-2 gains an axial hydroxy-group, and loses a *gauche* O-2/O-1 interaction while retaining a *gauche* O-2/O-3 interaction. The net effect seen is an overall shielding of the C-2 nucleus. C-3, which is β to O-2, exhibits a negative shift as expected.

(b) C-3 *Epimeric pairs* (*Table* 3). Comparison of the C-3 epimeric pairs, α-D-glucoside and α-D-alloside (4) and (1) and their 3-amino-derivatives (10) and (11) in which the substituent at C-2 is equatorial, and α-D-mannoside (6) and α-D-altroside (2) and their 3-amino-derivatives (13) and (12) in which the substituent at C-2 is axial, also confirms the assignments already made. On changing the substituent on C-3 from *eq* to *ax* a large

TABLE 3

C-3 Epimers (α-series); a negative sign represents an upfield shift

	$\Delta\delta_C$	C-1	C-2	C-3	C-4	C-5	C-6
C-2 *eq*	(1)—(4)	+0·3	−4·5	−1·7	−2·7	−5·1	+0·3
	(11)—(10)	+1·4	−4·6	−0·3	−2·7	−5·5	+0·2
C-2 *ax*	(2)—(6)	−0·1	−1·0	+0·8	−2·5	−5·1	+0·4
	(12)—(13)	−0·3	−0·6	+1·7	−3·5	−5·8	+0·3

[21] A. J. Jones, E. L. Eliel, D. M. Grant, M. C. Knoeber, and W. F. Bailey, *J. Amer. Chem. Soc.*, 1971, **93**, 4772.

shielding would be expected at C-5 due to the gain of a 1,3-diaxial interaction; this is observed (Table 3). Since all compounds are α-anomers, the shift at C-1 will be due mainly to a gain of a 1,3-diaxial interaction between O-1 and O-3, relative to that already present between O-1 and H-3. This effect has been shown to be small [3] and is so in all cases except that of the change from 3-amino-glucoside to 3-amino-alloside [(10) to (11)].

C-2 and C-4 are expected to show shifts also, but whereas that at C-4 is consistent throughout due to the fixed configuration at C-4, the shift at C-2 will depend on the orientation of the hydroxy-group at that position. When C-2 bears an equatorial substituent, it is affected only as a result of being β to O-3 and shielding is expected; this is observed in both cases. C-3 is affected in several ways: it gains an axial hydroxy-group and a 1,3-diaxial interaction between its axial OH and the axial proton on C-5, both of which should cause increased shielding, and the 1,3-diaxial interaction between its own proton and the axial oxygen atom on C-1 is changed to one between O-1 and O-3, a small effect. The overall effect is the expected shielding.

When the C-2 substituent is axial, C-2 is shielded by the axial hydroxy-group on the adjacent carbon and deshielded by loss of a *gauche* O-2/O-3 interaction. The resultant shift is small and negative. C-3 experiences an overall deshielding effect as a result of the gain of an axial hydroxy-group and 1,3-diaxial interactions between its own axial hydroxy-group and the axial oxygen atom on C-1 and the axial proton on C-5, all of which will cause a shielding of the C-3 carbon, as against loss of a *gauche* O-3/O-2 interaction and of a 1,3-diaxial interaction between its axial proton and the axial oxygen atom on C-1.

It appears from the shift observed at C-2 in changing from 3-deoxy-α-D-*ribo*-hexopyranoside (8) to 3-deoxy-α-D-*arabino*-hexopyranoside (9) that the deshielding caused by the loss of a *gauche*(*ax,eq*) interaction is greater than the shielding caused by acquisition of an axial in place of an equatorial hydroxy-group. The shift at C-2 on epimerisation at C-2 and C-3 of the α-*gluco* compound (4) and its 3-amino-derivative (10) implies that the shielding caused by a *gauche*(*ax,eq*) interaction is greater than that caused by a *gauche*(*eq,eq*) interaction.

Effect of O-*Substitution.*—Comparison of the ^{13}C n.m.r. spectrum of methyl 4,6-*O*-benzylidene-2-*O*-tosyl-α-D-alloside (15) with that of the corresponding diol (1) shows a marked deshielding of C-2 in the former compound of 6·7 p.p.m. and a slight shielding (1·9 p.p.m.) of C-1; C-3 and C-4 are only slightly affected. These effects of a sulphonyl ester have been studied in greater detail on simple model compounds.[22] In methyl 4,6-*O*-benzylidene-2,3-di-*O*-tosyl-α-D-altroside (16) C-2 and C-3 are deshielded relative to the corresponding diol (2), and C-1 and C-4 are both shielded.

The ^{13}C n.m.r. spectra of a series of 2,3-di-*O*-substituted methyl 4,6-*O*-benzylidene-α-D-glucosides have been obtained and assigned (see Table 4). In this series the signals due to the benzylidene aromatic carbon atoms are unaltered by substitution of the hydroxy-groups at C-2 and C-3 but are masked by the signals of the tosyl and benzoyl aromatic carbon atoms in compounds (20) and (22). C-5 and C-6 are also unaffected by the substitution and their signals remain at 62·5 ± 0·2 and 68·8 ± 0·2 p.p.m., respectively, throughout the series. The signals due to C-7 and the methoxy-carbon atom are also relatively unaltered, occurring at 101·7 ± 0·4 and 55·4 ± 0·4 p.p.m., respectively. In the di-*O*-mesyl and di-*O*-tosyl derivatives (19) and (20), C-2 and C-3 are deshielded relative to the diol, the mesyl groups causing greater deshielding than the tosyl groups. In view of the nearly identical deshielding upon tosylation or mesylation of the oxymethine carbon atom [22] this effect can be interpreted in terms of greater 1,2-interactions in the case of a tosylate than in the case of a mesylate. In both these compounds, C-1 and C-4 are shielded relative to the diol. This shielding is slightly greater at both C-1 and C-4 in the tosyl than in the mesyl derivative. In the di-*O*-acetyl and di-*O*-benzoyl derivatives (21) and (22), C-1 and C-4 are again shielded with respect to the diol but in these derivatives C-2 and C-3 are only very slightly shielded as a result of competing acetylation or benzoylation effects (deshielding) and increased *gauche* interactions causing shielding.[22] In the di-*O*-methyl derivative (23) C-2 and C-3 are markedly deshielded relative to the diol and resonate at even lower field than C-4, which is slightly shielded, as is C-1.

The shifts of C-2 and C-3 on acetylation, benzoylation, and methylation are similar to those quoted for other derivatives.[2,4,23,24] No data have been published until now on the effect of tosyl and mesyl groups but from the

TABLE 4

^{13}C N.m.r. shifts (downfield from Me_4Si) of derivatives of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside

Compound	R[1]	R[2]	R[3]	R[4]	R[5]	R[6]	C-1	C-2	C-3	C-4	C-5	C-6	C-7	OMe
(19) [a]	OMe	H	H	OMs	H	OMs	99·1	77·3	76·0	79·2	62·5	68·7	102·1	56·2
(20) [b]	OMe	H	H	OTs	H	OTs	98·6	76·0	74·3	79·1	62·5	68·6	102·0	55·9
(21) [c]	OMe	H	H	OAc	H	OAc	97·8	71·8	69·2	79·3	62·5	68·8	101·6	55·4
(22) [d]	OMe	H	H	OBz	H	OBz	98·0	72·6	69·7	79·5	62·7	68·9	101·6	55·5
(23) [e]	OMe	H	H	OMe	H	OMe	99·1	82·1 [f]	81·6 [f]	80·0 [f]	62·4	69·1	101·4	55·5

[a] δ_{Me} of mesyl at 38·8—39·1 p.p.m. [b] δ_{Me} of tosyl at 21·7 p.p.m. [c] δ_{Me} of acetate at 20·7 p.p.m.; δ_{CO} of acetate at 169·6—170·4 p.p.m. [d] δ_{CO} of benzoate at 167·7—168·3 p.p.m. [e] δ_{Me} of OMe at 59·5—60·5 p.p.m. [f] Values may be interchanged.

[22] G. Lukacs, M. Sangaré, A.-M. Sepulchre, S. D. Gero, and R. D. Guthrie, unpublished results.

[23] H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Robets, *J. Amer. Chem. Soc.*, 1969, **91**, 7445.

[24] G. W. Buchanan and J. B. Stothers, *Canad. J. Chem.*, 1969, **47**, 3605.

above studies it can be seen that these substituents cause marked deshielding of the oxymethine carbon atom relative to a hydroxy-group. The magnitudes of the shifts show that, in order to differentiate the signals of two hydroxylated carbon atoms, which occur close together, the spectrum of an *O*-methyl derivative of one of them would be most effective. However, either an *O*-mesyl or an *O*-tosyl derivative could also be used.

Other Compounds.—In the spectrum of methyl 4,6-*O*-benzylidene-3-deoxy-3-methylamino-α-D-altroside (**17**), the resonance of C-3 is shifted 8·8 p.p.m. downfield from that of C-3 in the 3-amino-derivative (**12**). Thus methylation of an amino-group has a similar effect to that of methylation of a hydroxy-group (see above).

C-3 of the 2-*O*-acetyl-3-azido-3-deoxy-α-altroside (**18**) is shielded with respect to the diol (**2**) by 10·3 p.p.m.; this shielding is less than that caused by an amino-group, in agreement with effects found from a study of simple t-butylcyclohexane derivatives.[22]

EXPERIMENTAL

All the substances studied were drawn from the University of Sussex collection of carbohydrate compounds. The spectra were run in 4 : 1 $CDCl_3$–MeOH on a Fourier transform spectrometer at 15·08 MHz. Chemical shifts are given with respect to tetramethylsilane (low-field positive).

One of us (E. C.) thanks the Schering Corporation of New Jersey for financial assistance.

[3/2092 *Received*, 12*th October*, 1973]