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THE ASSIGNMENT OF BENZYL METHYLENE CARBON RESONANCES OF PER-*O*-BENZYLATED METHYL FURANOSIDES: CORRELATION OF ASSIGNED CHEMICAL SHIFTS WITH FURANOSYL-RING STRUCTURE

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ABSTRACT

Benzyl methylene carbon resonances in perbenzylated methyl furanosides have been assigned by using a combination of INADEQUATE and ^{13}C–^{1}H shift-correlation n.m.r. spectroscopies. We find that one-bond carbon–carbon coupling constants between furanosyl-ring carbon atoms and the shifts of benzyl methylene carbon resonances are related to the relative orientation of substituents on the furanosyl rings. Re-examination of shift data for perbenzylated methyl pyranosides suggests that the same underlying phenomena similarly influence the shielding of pyranosyl-ring carbon atoms and their benzyl methylene carbon substituents.

INTRODUCTION

In recent studies, we and others have shown that the chemical shifts of the acetyl carbonyl carbon atoms and the benzyl methylene carbon atoms of per-*O*-acetylated and per-*O*-benzylated derivatives of aldopyranoses are sensitive to the structure of the pyranosyl ring[1–4]. In the case of the benzylated derivatives, the shifts of benzyl methylene carbon atoms appear to be influenced by their disposition with respect to the ring and by the disposition of neighboring substituents[1]. A change from an axial to equatorial disposition of the benzyl or neighboring benzyl substituents results in a substantial downfield shift in the benzyl methylene carbon resonance.

In the present report, we extend our studies to several per-*O*-benzylated methyl aldofuranosides. As was the case for the per-*O*-benzylated pyranose derivatives, we find that the shifts of benzyl methylene carbon resonances are sensitive to ring structure. Furthermore, we find that the same general empirically derived rules which can be used to predict shifts of furanosyl ring carbon and proton resonances[5–7] can also be of use in predicting shifts of benzyl methylene carbon resonances. Re-examination of data for benzylated pyranoses showed that there is

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a corresponding relationship between the shifts of benzyl methylene carbon atoms and pyranosyl-ring carbon atoms.

EXPERIMENTAL

Materials. — D-Xylose, D-arabinose, D-ribose, D-lyxose, D-fucose, trifluoroacetic acid, and Dowex-1 ion-exchange resin were obtained from Sigma Chemical Co. (St. Louis, MO). Methyl furanosides were prepared by stirring the sugars in 1:99 trifluoroacetic acid–methanol for 6–24 h at room temperature. This procedure yielded a higher percentage of furanosides than could be obtained by using the traditional methods of preparation[8]. The mixture of anomers obtained was separated on a column (2 × 100 cm) of Dowex-1 (OH^-) resin (400 mesh), using water as the eluant[9]. Per-*O*-benzylation was carried out as described previously[1], using a modification of the procedure of Hakomori[10] for the preparation of per-*O*-methylated carbohydrate derivatives.

N.m.r. spectral conditions. — Per-*O*-benzylated sugars were dissolved in $CDCl_3$ (1–1.5 g in 3 mL) containing 1% of Me_4Si. Normal F.t. and INADEQUATE[11] ^{13}C-n.m.r. spectra were acquired in the presence of broad-band decoupling at 4.7 T, using a JEOL FX-200 spectrometer. INADEQUATE experiments were carried out at 55° using a $\pi/2$-τ-π-τ-$\pi/2$-Δ-acq pulse-sequence, where τ and Δ were 5.2 ms and 2 μs respectively. A relaxation delay-time of 2 s was used. ^{13}C–^1H shift correlation spectra[11] were acquired on a Bruker AM-200 spectrometer using a spectral width of 1000 Hz in the F_2 (^{13}C shift) dimension and ±250 Hz in the F_1 (^1H shift) dimension (region of aromatic protons not included). The fixed delay-time, Δ_1, was set to 3.3 ms or to 55 ms, to emphasize short- and long-range coupling, respectively. Each spectrum was an average of 8 acquisitions when Δ_1 was 3.3 ms, or 64 acquisitions when Δ_1 was 55 ms. A relaxation delay of 2 s was used. These experiments were carried out at ambient probe-temperature (~30°) in the presence of broad-band decoupling.

Pyranosyl-ring carbon assignments and ^{13}C–^{13}C coupling constants were determined by fitting experimental INADEQUATE spectra to simulated spectra generated by LAOCOON[12] running on an IBM PC-compatible microcomputer.

RESULTS AND DISCUSSION

The structures of those per-*O*-benzylated methyl furanosides studied in the present investigation are shown: methyl 2,3,5-tri-*O*-benzyl-α- and -β-D-xylofuranoside (**1a** and **1b**), methyl 2,3,5-tri-*O*-benzyl-α- and -β-D-arabinofuranoside (**2a** and **2b**), methyl 2,3,5-tri-*O*-benzyl-β-D-ribofuranoside (**3**), methyl 2,3,5-tri-*O*-benzyl-α-D-lyxofuranoside (**4**), and methyl 2,3,5-tri-*O*-benzyl-α- and -β-D-fucofuranoside (**5a** and **5b**). The suffix MBzl is used throughout to denote benzyl methylene carbon substituents of furanosyl-ring carbon atoms (*e.g.*, C-2MBzl denotes the benzyl methylene carbon atom attached to O-2).

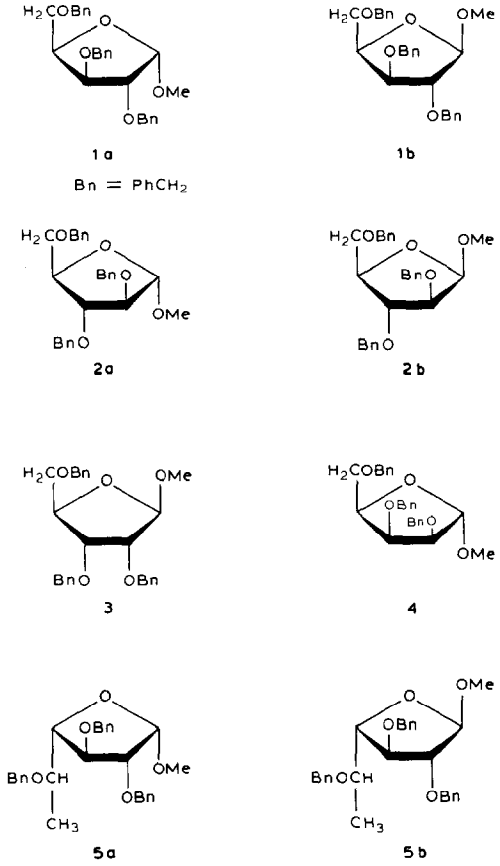

Fig. 1 shows the region of the proton-decoupled, ^{13}C-n.m.r. spectrum containing the benzyl methylene and the C-5 methylene carbon resonances of **1a–2b**. With the exception of peak 1, which has nearly the same shift in the spectra of all four compounds, the pattern of resonances in each of the four spectra is unique. Recent investigations in our laboratory have suggested that the benzyl methylene carbon resonances of per-*O*-benzylated and the carbonyl carbon resonances of per-*O*-acetylated mono- and oligo-saccharide derivatives of known structure can be used as an aid in the identification of unknown derivatives, once a library of shifts has been established[1,2]. It should be noted that the pattern of resonances in the spectrum of **1b** (see Fig. 1B) closely resembles the pattern of resonances observed in the spectrum of **2a** (Fig. 1C). Likewise, the pattern of resonances seen in the spectrum of **1a** (Fig. 1A) more closely resembles the corresponding pattern seen in the spectrum of **2b** (Fig. 1D) than the pattern of resonances seen in the other two spectra shown. Reference to the structures of these compounds shows that **1b** and **2a** have *cis*-1,2 substituents, whereas **1a** and **2b** have *trans*-1,2 substituents. This suggests that the relative orientation of benzyl methylene carbon substituents may be a factor in determining their chemical shifts.

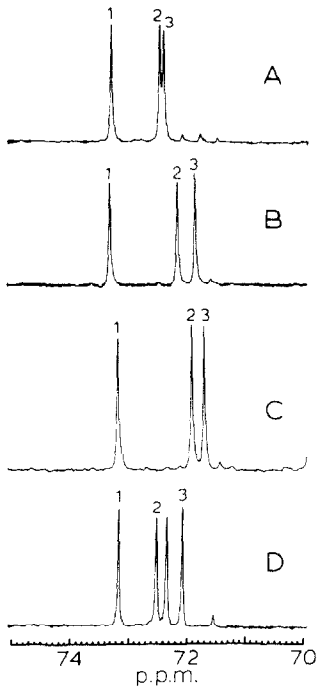

Fig. 1. 50-MHz, proton-decoupled ^{13}C-n.m.r. spectra of (A) **1a**, (B) **1b**, (C) **2a**, and (D) **2b**. Spectra were acquired at ambient temperature on samples (300 mg/mL) in $CDCl_3$. Numbered resonances are assigned to benzyl methylene carbon atoms (assignment data summarized in Table III). The unnumbered resonance in spectrum 1D can be assigned to C-5. The very low intensity resonance in the upfield portion of each of the spectra arises from unidentified impurities in the samples.

Assignment of resonances of aglycon methyl carbon and C-1 through C-6. — Furanosyl-backbone carbon resonances were assigned by spectral simulation of INADEQUATE spectra. As an example, Fig. 2 shows the normal, proton-decoupled, ^{13}C-n.m.r. spectrum, the INADEQUATE spectrum, and the simulated INADEQUATE spectrum of **1b** in the region containing resonances arising from C-2 through C-4. The INADEQUATE spectrum shows the out-of-phase couplets arising from one-bond, ^{13}C–^{13}C coupling interactions. Couplets of the C-1 resonance (not shown) and one set of couplets associated with peak 1 share a unique coupling constant of 47.6 Hz. On this basis, peak 1 can be assigned to C-2. The resonance arising from C-3 was assigned by obtaining the best fit between the remaining couplet of peak 1 and one set of couplets associated with either peak 3 or 4. This pairwise fitting procedure was continued until the best overall fit to the experimental data was obtained, using as experimentally determined parameters the shifts of the resonances in the normal ^{13}C-n.m.r. spectrum. Shifts and coupling constants determined in this manner are summarized in Tables I and II.

Assignment of benzyl methylene carbon resonances. — Benzyl methylene carbon resonances can be correlated to previously assigned furanosyl-ring carbon

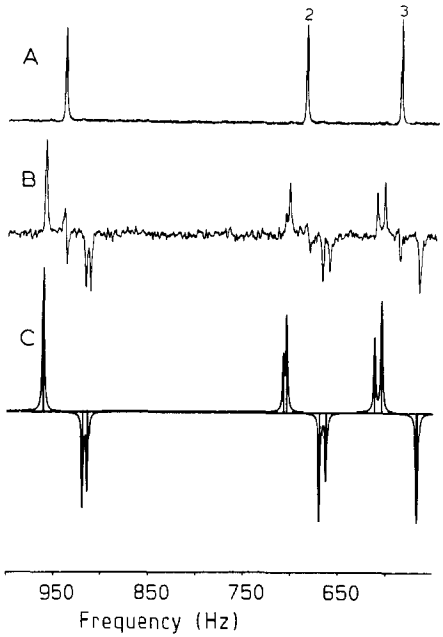

Fig. 2. (A) 50-MHz, proton-decoupled ^{13}C-n.m.r. spectrum of **1b** in $CDCl_3$. [Only the furanosyl-ring carbon resonances arising from C-2, C-3, and C-4 are shown.] (B) INADEQUATE spectrum of **1b**. (C) Computer-simulated INADEQUATE spectrum of **1b**, assuming resonances 1, 2, and 3 can be assigned to C-2, C-3, and C-4.

TABLE I

CHEMICAL SHIFTS OF RING CARBON ATOMS OF PER-*O*-BENZYLATED METHYL FURANOSIDES[a]

Compound		*Assigned shift (p.p.m.)*						
		C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Me*
α-Xyl	(**1a**)	100.45	83.83	81.47	75.83	69.29		55.12
β-Xyl	(**1b**)	108.04(106.7)	86.75(87.5)	83.86(81.8)	81.53(79.2)	69.70(70.4)		55.42
α-Ara	(**2a**)	107.28(106.7)	88.10(87.8)	83.42(82.8)	80.91(81.5)	69.82(70.1)		54.87
β-Ara	(**2b**)	101.62(100.8)	84.15(84.1)	83.25(81.5)	80.33(78.5)	72.33(70.6)		54.84
β-Rib	(**3**)	106.28(105.4)	79.65(81.4)	78.35(76.2)	80.42(79.5)	71.25(70.6)		54.92
α-Lyx	(**4**)	106.36(106.2)	82.49(83.5)	77.87(78.0)	78.19(77.0)	69.61(69.6)		55.50
α-Fuc	(**5a**)	101.10(100.5)	84.45(83.8)	81.56(81.5)	83.54(75.8)	76.85(69.3)	15.42	54.78
β-Fuc	(**5b**)	106.78(106.7)	88.16(87.5)	83.10(81.8)	84.10(79.2)	73.53(70.4)	15.80	54.52

[a]Assignments were determined by fitting experimental INADEQUATE spectra, using LAOCOON[12]. All chemical shifts are reported in p.p.m. with respect to 1% of Me_4Si added as an internal reference. Numbers in parentheses were calculated from data of Ritchie *et al.*[5] determined for methyl furanosides in D_2O. Compound **1a** was used as a reference compound in the calculations.

TABLE II

ONE-BOND CARBON–CARBON COUPLING-CONSTANTS FOR PER-*O*-BENZYLATED METHYL FURANOSIDES[a]

Compound		*Coupling constant (Hz)*			
		$J_{C-1,C-2}$	$J_{C-2,C-3}$	$J_{C-3,C-4}$	$J_{C-4,C-5}$
α-Xyl	(**1a**)	44.8	42.6	39.6	45.3
β-Xyl	(**1b**)	47.6	42.0	38.3	44.6
α-Ara	(**2a**)	48.3	42.3	39.0	44.6
β-Ara	(**2b**)	45.0	41.9	40.1	44.1
β-Rib	(**3**)	46.8	39.2	39.6	43.6
α-Lyx	(**4**)	47.7	38.9		45.9
α-Fuc	(**5a**)	44.6	39.8	40.4	43.7
β-Fuc	(**5b**)	48.3	42.6		44.8

[a]Data shown were determined by the best fit to experimental data, using LAOCOON[12] spectral simulation. Coupling constants not listed could not be determined, due to strong coupling resulting in cancellation of the strong negative and positive intensities arising from couplet pairs in the experimental INADEQUATE spectrum.

resonances by virtue of the common coupling of both types of carbon atom to the same furanosyl-ring proton. This rather indirect method for assigning benzyl methylene carbon resonances has the advantage that the proton spectrum need not be assigned, eliminating potential problems associated with assigning degenerate or strongly coupled proton resonances[1,2] or both. Fig. 3A shows the ^{13}C–^{1}H shift-

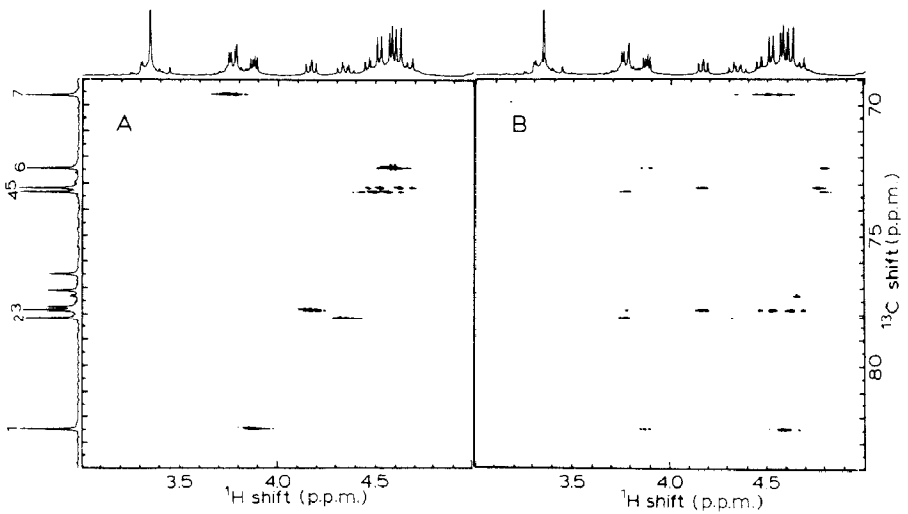

Fig. 3. ^{13}C–^{1}H Shift-correlation contour spectra of **4** in which data were collected with (A) a delay time (Δ_1) of 3.2 ms. [Cross-peaks arise between carbon atoms and their attached protons.] (B) A delay time (Δ_1) of 55 ms. [The apparent crosspeaks between 4.7 and 4.9 p.p.m., corresponding to resonances 4–6, are spectral artifacts. All other crosspeaks arise from carbon atoms coupled to protons two or three bonds away. Normal F.t., ^{13}C and ^{1}H spectra are shown along the vertical and horizontal axes. The group of three equally spaced resonances between 76 and 78 p.p.m. arises from the solvent ($CDCl_3$).]

correlation spectrum of **4**, where the fixed delay-time in the pulse sequence has been selected to emphasize short-range ^{1}H–^{13}C coupling interactions[11]. Resonances previously assigned to C-2, C-4, C-3, and C-5 in the ^{13}C-n.m.r. spectrum (peaks 1–3 and 7) are seen to correlate to proton resonances at about 3.85, 4.35, 4.15, and 3.75 p.p.m., whereas benzyl methylene carbon resonances (peaks 4–6) correlate to protons showing AB splitting patterns between about 4.4 and 4.7 p.p.m. The ^{13}C–^{1}H shift-correlation map in Fig. 3B was acquired by using fixed delays which emphasize correlations arising from long-range couplings. Peaks 1 and 3 in the carbon spectrum (previously assigned to C-2 and C-3) are now seen to correlate to the same methylene protons as peaks 6 and 5 in Fig. 3A. Hence, peaks 5 and 6 can be assigned to C-3MBzl and C-2MBzl. By elimination, peak 4 can be assigned to C-5MBzl. The shifts of all benzyl methylene carbon atoms assigned in this manner are summarized in Table III.

Structural factors affecting chemical shifts of assigned furanosy-ring carbon resonances. — Furanosyl proton and carbon resonance shifts have been shown to depend on the relative orientation of ring substituents[5–7]. Resonances arising from neighboring carbon atoms having *cis*-hydroxyl groups lie 5–7 p.p.m. upfield of neighboring carbon atoms with *trans* substituents. To a lesser extent, other longer-range *cis* interactions in the ring cause upfield shifts as well. Ritchie *et al.*[5] quantitatively determined the contribution that each *cis* interaction makes to the shift of each carbon resonance by fitting shift-data obtained from eight methyl pentofuranosides. Although it is not possible to reevaluate these contributions for per-*O*-benzylated methylfuranosides due to the limited number of compounds studied, the coefficients previously determined for underivatized compounds can be used to calculate expected carbon-resonance shifts. These shifts are shown in parentheses

TABLE III

ASSIGNED SHIFTS OF BENZYL METHYLENE CARBON ATOMS OF PER-*O*-BENZYLATED METHYL FURANOSIDES[a]

Compound		*Chemical shift (p.p.m.)*		
		C-2MBzl	*C-3MBzl*	*C-5MBzl*
α-Xyl	(**1a**)	72.47	72.47	73.32
β-Xyl	(**1b**)	71.77	72.06	73.29
α-Ara	(**2a**)	71.86	72.09	73.35
β-Ara	(**2b**)	72.53	72.21	73.21
β-Rib	(**3**)	72.21	72.32	73.06
α-Lyx	(**4**)	72.44	73.18	73.34
α-Fuc	(**5a**)	72.38	72.03	71.04
β-Fuc	(**5b**)	71.65	71.95	71.10

[a]Assignments were made indirectly by correlating the benzyl methylene carbon atoms to assigned ring-carbon atoms by observing the shifts of proton resonances to which both types of carbon atom are coupled. These correlations were made by using ^{13}C–^{1}H shift-correlation spectra, as described in the text.

in Table I, the shifts of **1a** having been taken as a reference. Although the choice of a particular reference compound is immaterial to the overall agreement between experimental and calculated shifts, the agreement observed for any particular atom type and compound depends on the reference. For example, nearly all of the calculated shifts for C-4 appear substantially lower than those observed. The reason for this might be an anomalously shielded C-4 atom of the reference compound **1a**. Alternatively, the magnitudes of *cis* contributions to the C-4 chemical-shift for underivatized methyl furanosides may differ substantially from those of per-*O*-benzylated derivatives. The differences between experimental and calculated values are probably influenced by both effects. The fit could probably be improved for C-4 of compounds **1b–4** by use of a better choice of coefficients, as the differences are less than ~2 p.p.m. On the other hand, the 7–8-p.p.m. difference between calculated and experimental shifts for C-4 of **5a** and **5b** is probably due to the inductive effect of the 5-*C*-methyl group (C-6). Excluding compounds **5a** and **5b**, as they are structurally different from the pentofuranoside derivatives, there is a standard deviation between experimental and calculated values of 1.2, 1.1, 1.8, and 1.6 p.p.m. for C-1, C-2, C-3, and C-4. These deviations seem reasonable if the fact that the calculated values were based on *cis* contribution determined for a completely different set of compounds is taken into account. They suggest that the same underlying structural features determine the observed shifts both in per-*O*-benzylated and underivatized methyl furanosides.

One-bond carbon–carbon coupling-constants in per-*O*-benzylated methyl furanosides appear to be determined by the same underlying phenomena that affect the shielding of furanosyl-ring carbon atoms. In underivatized furanosides, carbon atoms bearing alkylated hydroxyl groups are deshielded[5]. Hence, C-1, which has two alkylated hydroxyl groups, lies 15–20 p.p.m. downfield of those with only one benzylated hydroxyl group. The C-2 is also atom deshielded by the second alkylation at C-1 (a β-effect) and, for all compounds studied, gives rise to a resonance lying downfield of resonances arising from C-3 and C-4. The shielding of C-3 relative to that of C-4 is influenced by *cis* interactions of other substituents in the ring. For compounds **1a–2b**, C-4 is more shielded than C-3, whereas for the remaining compounds studied, the reverse is true. Hence, δ(C-1) > δ(C-2) > δ(C-3) > δ(C-4) for **1a–2b**, and δ(C-1) > δ(C-2) > δ(C-4) > δ(C-3) for **3–5b**. Consistent with these trends, $J_{C\text{-}1,C\text{-}2} > J_{C\text{-}2,C\text{-}3} > J_{C\text{-}3,C\text{-}4}$ for **1a–2b** and $J_{C\text{-}1,C\text{-}2} > J_{C\text{-}3,C\text{-}4} > J_{C\text{-}2,C\text{-}3}$ for **3** and **5a**. One-bond ^{13}C–^{13}C coupling-constants of the same type appear to correlate with the sum of the shifts of the two atoms coupled to one another. This is shown graphically in Fig. 4, where $J_{C\text{-}1,C\text{-}2}$, $J_{C\text{-}2,C\text{-}3}$, and $J_{C\text{-}3,C\text{-}4}$ are shown to increase with the sum of chemical shifts, and $J_{C\text{-}4,C\text{-}5}$ is shown to decrease. Similar correlations have been seen between $^3J_{H\text{–}H}$ and chemical shifts of neighboring furanosyl-ring protons[7]. On the other hand, one-bond carbon–carbon coupling-constants in pyranose-ring systems appear to be influenced by factors other than pairwise shielding[13–15].

Structural factors affecting chemical shifts of assigned benzyl methylene carbon

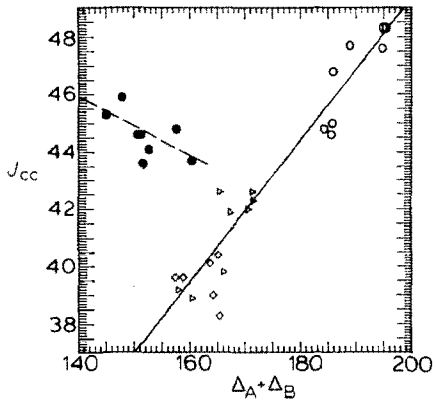

Fig. 4. The sum of chemical shifts of atom pairs *vs.* one-bond carbon–carbon coupling-constants observed for compounds **1a–5b**. Points in the Figure represent data for C-1,C-2 (○), C-2,C-3 (△), C-3,C-4 (◇), and C-4,C-5 (●). Lines represent linear, least-squares fits. The fits yield correlation coefficients of 0.96 and 0.61 for the C-1 through C-4 data and the C-4,C-5 data, respectively.

resonances. — Table III shows that the shifts of the C-5MBzl resonances of all of the per-*O*-benzylated methyl pentofuranoside derivatives occur between about 73.1 and 73.3 p.p.m. Plots of the chemical shifts of these resonances *vs.* the shifts of the C-5 resonances failed to reveal any significant correlations. It may therefore be concluded that the C-5MBzl atoms are far enough removed from the structure of the pentofuranosyl ring as not to be significantly affected by the same *cis–trans* interactions that appear to govern the shifts of other furanosyl-ring carbon resonances. However, the shielding of the C-5MBzl carbon atoms is influenced by the inductive effect of a 5-*C*-methyl substituent, as evidenced by the increased shielding of C-5MBzl in **5a** and **5b**.

Fig. 5A shows a plot of the shifts of the C-2MBzl and C-3MBzl resonances *vs.* the shifts of neighboring C-2 and C-3 atoms. With the exception of two data points, one arising from the shifts of the C-2, C-2MBzl pair of **3** (at 79.7 and 72.2 p.p.m.) and the other from the shifts of the C-3, C-3MBzl pair of **3** (at 78.4 and 72.3 p.p.m.), the data appear to correlate well. A linear, least-squares fit yielded correlation coefficients of 0.93 and 0.91 for the C-2MBzl and C-3MBzl data (σ_y = 0.2 p.p.m. for both sets). Hence, it appears that, for compounds other than the per-*O*-benzylated methyl β-D-ribofuranoside, the structure of the furanose ring affects the shielding of furanosyl-ring carbon atoms and benzyl methylene carbon atoms similarly. There are no obvious structural reasons why the same correlations do not hold for C-2MBzl and C-3MBzl of the β-D-ribofuranoside derivative. Both **3** and **4** have *cis*-2,3 and *trans*-1,2 and -1,3 benzyl substituents. If the small effect that the relative orientation of C-5 has on the shifts of C-2 and C-3 in other derivatives is considered, there is no obvious reason why the different orientation of C-5 in **3** and **4** should produce the type of deviation observed.

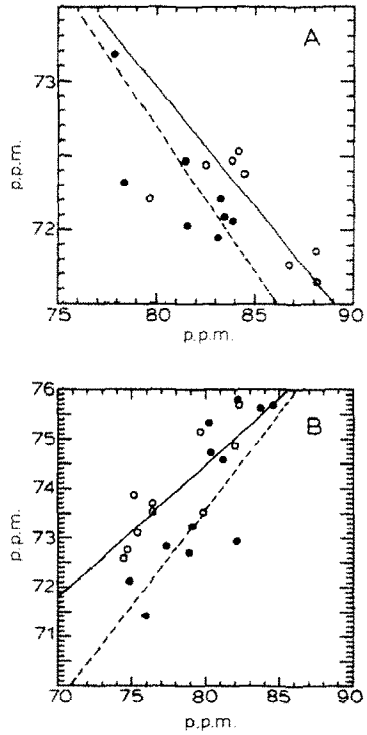

Fig. 5. (A) The shifts of C-2 (○) and C-3 (●) resonances *vs.* those of C-2MBzl and C-3MBzl for compounds **1a–5b**. [Anomalous data points at (79.7, 72.2 p.p.m.) and (78.4, 72.3 p.p.m.) arise from C-2 and C-3 of **3**. Lines in the Figure represent linear, least-squares fits, excluding data poins for **3**.] (B) Shifts of C-2 (○) and C-3 (●) resonances of per-*O*-benzylated pyranoses *vs.* those of C-2MBzl and C-3MBzl. [Data were obtained from the twelve compounds in ref. 1. Only ten C-2 data-points are present, as two of these twelve compounds are substituted at C-2 with groups other than benzyl.]

Fig. 5B shows a plot of the chemical shifts of C-2 and C-3 resonances *vs.* the shifts of C-2MBzl and C-3MBzl resonances taken from data for per-*O*-benzylated methyl pyranosides[1]. Although the data do not appear to correlate as well as in the case of the furanosides (correlation coefficients of 0.86 and 0.83 from linear, least-squares fit to C-2MBzl and C-3MBzl data), the structure of the pyranosyl ring again appears to affect the shielding of ring-carbon atoms and benzyl methylene carbon atoms similarly. Similar plots failed to reveal a correlation between the shielding of C-4 and C-6 and their benzyl methylene carbon substituents. In the case of the C-6 data, the C-6MBzl is far enough removed from the ring structure that the range of resonance shifts observed is quite small (0.2 p.p.m.). It is unclear why C-4MBzl resonance shifts do not correlate with the shifts of C-4 resonances.

CONCLUSIONS

We have shown that the same underlying phenomena are responsible for the

electronic shielding of furanosyl-ring carbon atoms and their benzyl methylene carbon substituents. These phenomena can be predicted from the relative orientation of substituents on the furanosyl ring. The reexamination of shift data for benzylated pyranosides revealed that the shielding of pyranosyl-ring carbon atoms and their benzyl methylene carbon substituents are also affected by a common influence. It is surprising that the same underlying phenomena influence the magnitude of one-bond carbon–carbon coupling-constants between carbon atoms of the furanosyl ring. This is especially true in light of the fact that no single empirical rule can be derived which relates ^{13}C–^{13}C coupling-constants to structural features of pyranoses.

Finally, it may be noted that the correlation that exists between the shifts of ring-carbon atoms and their benzyl methylene carbon substituents cannot be generalized to other substituted mono- and oligo-saccharides. No correlation seems to exist between the chemical shifts of pyranosyl-ring carbon resonances and those of their carbonyl substituents in per-*O*-acetylated derivatives[2]. Such a correlation does exist, however, between the shifts of carbonyl carbon atoms and those of pyranosyl-ring protons.

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