# ROTAMERIC BEHAVIOUR OF METHOXY GROUPS IN SOME ALDOPYRANOSES

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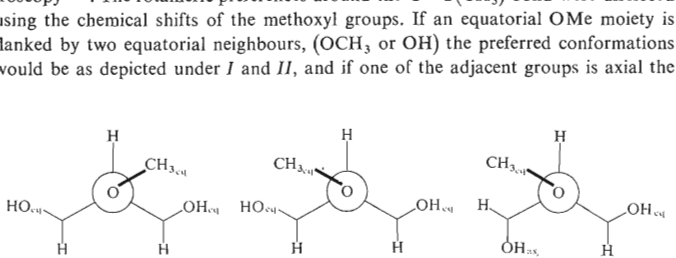
Received February 28th, 1977

Through the determination of the chemical shift increments for the ring protons in pyranoses at the geminal and vicinal positions of a methoxy grouping it is possible to obtain qualitative insight about the rotameric states of the latter. This is exemplified on methyl α- and -β-D-glucopyranoside, 2-O-methyl-α- and -β-D-glucopyranose, 3-O-methyl-β-D-gulopyranose, 4-O-methyl-α- and β-L-arabinopyranose and methyl 2-O-methyl-α- and -β-D-glucopyranoside. It is stated that an H-5 axial proton is much less deshielded by an axial methoxy group at the anomeric position than by the hydroxyl function. A small shielding for protons involved in $H(g^+, g^-, g^-)CH_3$ or $H(g^-, g^+, a)CH_3$ conformational fragments ($\delta$-effect) seems to occur.

Partially methylated sugars have been investigated both by $^1$H- and $^{13}$C-NMR spectroscopy[1–9]. The rotameric preferences around the C—O($CH_3$) bond were disclosed using the chemical shifts of the methoxyl groups. If an equatorial OMe moiety is flanked by two equatorial neighbours, ($OCH_3$ or OH) the preferred conformations would be as depicted under *I* and *II*, and if one of the adjacent groups is axial the

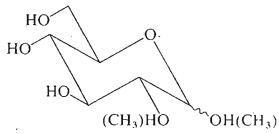



*I* *II* *III*

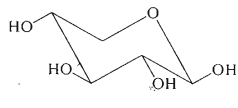
preferred rotamer would be *III* (ref.[1,7–9]). Also, a relation between $^1$H- and $^{13}$C--methoxy shifts has been proposed[7,8]. Chemical shifts for the ring protons of permethylated pyranoses have been reported[8] without interpreting these in light of possible rotameric distribution of the methoxy substituents. Rathbone[3,4] has studied the

changes of ring proton chemical shifts with the position of methylation in partially methylated D-galactosides.

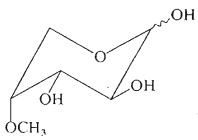
We apply now the earlier proposed[10] increment values, as caused by methoxy groups on protons in geminal and vicinal position on some partially methylated pyranoses (Scheme 1; methyl α- and β-D-glucopyranoside, 2-O-methyl-α- and -β-D-glucopyranose, methyl 2-O-methyl-α- and -β-D-glucopyranoside, 4-O-methyl-α- and -β-L-arabino pyranose and 3-O-methyl-β-D-gulopyranose).



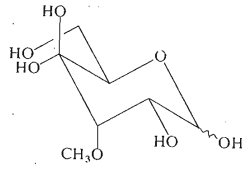

D-glucopyranose derivatives




β-D-xylopyranose




4-O-$CH_3$-L-arabino-pyranose ($^1C_4$-form)




3-O-$CH_3$-D-gulopyranose

SCHEME 1

The results show that it is easy to interpret qualitatively the observed influences in light of the conformational behaviour of methoxy groups around the C—O($CH_3$) bond, but that these preferred rotameric states differ sometimes somewhat from the earlier findings from the studies of the methoxy shifts[19].

## EXPERIMENTAL

The synthesis of methyl 2-O-methyl-α- and -β-D-glucopyranoside have been described[11] as well as the synthesis of 4-O-methyl-L-arabinopyranose[12]. The synthesis of 2-O-methyl-D-glucose was described[13]. 3-O-Methyl-α,β-D-gulopyranose was a commercial product (SEFOCHEM, Israel). It consists of a mixture of α-, and β-anomers, in which the amount of the α-isomer was too low to permit the extraction of precise data. Spectra were taken in $D_2O$ with trimethylsilylpentane-

sulfonic acid (TSP) as the internal reference on a VARIAN HR 300 MHz, equipped with homo INDOR facilities (SC 8525-2 decoupler). Simulations of some of the higher order spin system patterns were performed by SIMEQ 16/11 programme.

## RESULTS AND DISCUSSION

*β- and γ-Increment values*: It is known that a methyl[14] or hydroxyl[15] substituent causes an upfield displacement of a synclinal ring proton (−0·2/−0·3 ppm for a *syn--cis* and −0·0$_4$ ppm for a *syn-trans* methyl[14]) but a downfield shift of an antiperiplanar ring proton (+0·3 ppm for methyl). The largest upfield effect in *syn-cis* relations are met when eclipse occurs. For a longer chain substituent the shift effects on geminal protons are consistent[10] with cumulative α-, β- and γ-effects, whereby not only the first, but also the subsequent β- and γ-atoms of that side chain must be considered. Therefore these shift contributions depend on the rotational state of the side chain, *e.g.* of a methoxy group. In 1,3-dioxanes, these effects were found[16,17] to be rather sensitive to the substitution pattern, *e.g.* −0·12 to −0·43 ppm for *syn-cis*, +0·0$_2$ to −0·14 ppm for *syn-anti* and +0·15 to +0·18 ppm for antiperiplanar dispositions. We have collected in Table I the known γ-effects (or 1,3-effects) of a

TABLE I

Chemical Shift Increments (in ppm[a]) Caused by a Methyl-Group in Methyl-Cyclohexane (*A*), 2-Methyl-substituted 1,3-Dioxanes (*B*) and 4-Methyl-substituted 1,3-Dioxanes (*C*)

| 1,3 Effect | *A* (ref.[15]) | *B* (ref.[17]) | *B* (ref.[16]) | *C* (ref.[17]) | *C* (ref.[16]) |
|---|---|---|---|---|---|
| H($g^-$, *a*)CH$_3$<br>H($g^+$, *a*)CH$_3$ | +0·07 | +0·01 | +0·05 | +0·03 | 0 |
| H(*a*, $g^-$)CH$_3$<br>H(*a*, $g^+$)CH$_3$ | −0·26 | −0·16 | – | −0·22 | −0·25 |
| H(*a*, *a*)CH$_3$ | −0·03 | −0·03 | +0·03 | −0·02 | +0·03 |
| H($g^+$, $g^+$)CH$_3$<br>H($g^-$, $g^-$)CH$_3$ | – | −0·13/−0·30[b] | – | – | – |
| H($g^+$, $g^-$)CH$_3$<br>H($g^-$, $g^+$)CH$_3$ | +0·25 | +0·20 | +0·25 | +0·17 | +0·39 |

[a] Positive signs for displacements to lower field. [b] Values extracted from different 1,3-dioxane derivatives, including spiro-derivatives.

TABLE II

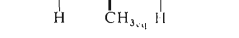
Chemical Shifts[a] of Methyl α- and -β-D-Glucopyranosides, 2-O-Methyl-α- and -β-D-Glucopyranoses and Methyl 2-O-Methyl-α- and -β-Glucopyranosides (in $D_2O$ *vs* TSP)

| Compound | H-1 | H-2 | H-3 | H-4 | H-5 | H-6A | H-6B | OMe-1 | OMe-2 |
|---|---|---|---|---|---|---|---|---|---|
| β-D-Glucopyranose | 4·65 | 3·27 | 3·45 | 3·35 | 3·42 | 3·89 | 3·72 | — | — |
| α-D-Glucopyranose | 5·23 | 3·50 | 3·71 | 3·36 | 3·82 | 3·83 | 3·77 | | |
| Methyl β-D-glucopyranoside | 4·38 | 3·26 | 3·51 | 3·38 | 3·47 | 3·93 | 3·73 | 3·60 | — |
| | (−0·27) | (−0·01) | (+0·06) | (+0·03) | (+0·05) | | | | |
| Methyl α-D-glucopyranoside | 4·80 | 3·56 | 3·68 | 3·40 | 3·65 | 3·85 | 3·75 | 3·45 | — |
| | (+0·15) | (+0·29) | (+0·23) | (0·05) | (+0·23) | | | | |
| | \|−0·43\| | \|+0·06\| | \|−0·03\| | \|+0·04\| | \|−0·17\| | | | | |
| 2-O-Methyl-β-D-glucopyranose | 4·65 | 3·00 | 3·56 | 3·41 | 3·44 | 3·89 | 3·72 | — | 3·52 |
| | (−) | (−0·27) | (+0·11) | (+0·06) | (+0·02) | | | | |
| 2-O-Methyl-α-D-glucopyranose | 5·50 | 3·26 | 3·73 | 3·43 | 3·62 | 3·84 | 3·76 | — | 3·43 |
| | (−0·15) | (−0·01) | (+0·28) | (+0·08) | (+0·20) | | | | |
| | \|+0·27\| | \|−0·24\| | \|+0·02\| | \|+0·07\| | \|−0·20\| | | | | |
| Methyl 2-O-methyl-β-D-glucopyranoside | 4·42 | 3·02 | 3·54 | 3·39 | 3·44 | 3·92 | 3·72 | 3·58 | 3·58 |
| | (−0·23) | (−0·25) | (+0·09) | (+0·04) | (+0·02) | | | | |
| Methyl 2-O-methyl-α-D-glucopyranoside | 5·05 | 3·29 | 3·69 | 3·42 | 3·81 | 3·88 | 3·76 | 3·48 | 3·43 |
| | (−0·60) | (+0·02) | (+0·24) | (+0·07) | (+0·39) | | | or 3·43 | 3·48 |
| | \|−0·18\| | \|−0·21\| | \|−0·02\| | \|+0·06\| | \|−0·01\| | | | | |

[a] ( ) is *vs* β-D-glucopyranose and \| \| is *vs* α-D-glucopyranose.

methyl group, wherefore the observed effects in 2- or 4-methyl-substituted 1,3-dioxanes (*B*) and (*C*) are perhaps the best values suited for the present purpose (Table I). We have gathered in Tables II – V the $^1$H-NMR parameters of the pyranoses relevant to the present discussion, obtained at 300 MHz.

C—$OCH_3$ *Rotamers in* 2-O-*methyl*-β-D-*glucopyranose*: Compared to β-D-glucopyranose itself, the following increments (in ppm) are found after methylation 0·0 (H-1), −0·27(H-2) and +0·11(H-3). The three rotameric states for 2-$OCH_3$ are displayed in (*IVA* – *IVC*) together with the relative configuration of the fragments under consideration. The upfield shift of H-2 and the downfield shift on H-3 exclude




*IVA* H-2(*app*)$CH_3$
H-*1*($g^+g^-$)$CH_3$
H-*3*($g^-g^-$)$CH_3$


*IVB* H-2(sc)$CH_3$
H-*1*($g^+g^+$)$CH_3$
H-*3*($g^-a$)$CH_3$


*IVC* H-2(sc)$CH_3$
H-*1*($g^+a$)$CH_3$
H-*3*($g^-g^-$)$CH_3$

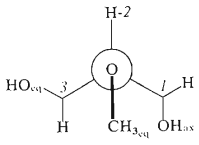
*IVA*. However for both *IVB* and *IVC* forms one would expect different increments than those observed. H-3 in *IVB* and H-1 in *IVC* are characterized by a H($g$,$a$)$CH_3$

TABLE III
Coupling Constants in Hz

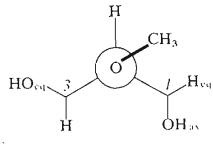
| Compound | *J*(1,2) | *J*(2,3) | *J*(3,4) | *J*(4,5) | *J*(5,6A) | *J*(5,6B) | *J*(6A, 6B) |
|---|---|---|---|---|---|---|---|
| β-D-Glucopyranose | 7·9 | 9·1 | 9·0 | 9·8 | 2·0 | 5·8 | −12·0 |
| α-D-Glucopyranose | 3·7 | 10·0 | 8·8 | 9·8 | 2·0 | 5·8 | −12·0 |
| Methyl β-D-glucopyranoside | 7·8 | 9·4 | 8·8 | 10·0 | 2·1 | 5·8 | −12·3 |
| Methyl α-D-glucopyranoside | 3·8 | 10·0 | 8·8 | 9·8 | 2·2 | 5·4 | −12·3 |
| 2-O-Methyl-β-D-glucopyranose | 7·9 | 9·2 | 9·0 | — | 1·8 | 5·6 | −12·2 |
| 2-O-Methyl-α-D-glucopyranose | 3·6 | 9·8 | 8·8 | 9·8 | 2·2 | 5·6 | −12·4 |
| Methyl 2-O-methyl-β-D-glucopyranoside | 7·9 | 9·2 | 8·8 | 9·6 | 1·8 | 5·6 | −12·2 |
| Methyl 2-O-methyl-α-D-glucopyranoside | 3·6 | 9·8 | 9·0 | 10·0 | 2·4 | 5·4 | −12·3 |

conformational arrangement (expected to result in a very small downfield effect) while H-1 in *IVB* and H-3 in *IVC* should suffer from an upfield effect ($g^+$, $g^+$ relation). Only an admixture of all three forms *IVA* – *IVC* may well explain the experimental data, with *IVB* being the preponderant rotamer. The presence of *IVA* as a minor component would explain the downfield shift on H-3. From $^{13}$C-NMR studies it has been concluded[18] that *IVB* and *IVC* are the sole rotamers present.

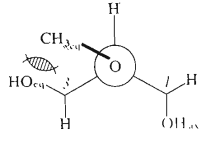
C—$OCH_3$ *Rotamers in* 2-O-*methyl*-α-D-*glucopyranose*: The increments are +0·27(H-1), −0·24(H-2) and +0·02(H-3). Out of the three rotamers *VA* – *VC*, *VA* may immediately be discarded as an important contributor because the substantial




*VA* H-2(*app*)$CH_3$
H-1($g^-g^-$)$CH_3$
H-3($g^+g^-$)$CH_3$

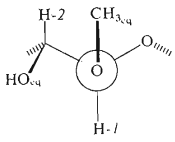



*VB* H-2(sc)$CH_3$
H-1($g^-g^+$)$CH_3$
H-3($g^-a$)$CH_3$

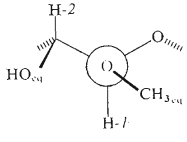



*VC* H-2(sc)$CH_3$
H-1($g^-a$)$CH_3$
H-3($g^-g^-$)$CH_3$

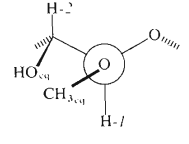
downfield effect for H-2 would be unlikely. Also the effect on H-3 would not be readily explained. Although considerations of the β-effects allow *VB* and *VC* to be good candidates, the latter is less probable because of an expected *g*, *a* effect to be almost zero on H-1; and H-3 would rather become shielded ($g^-$, $g^-$ effect). The data agree well with the *VB* rotamer as the sole species present. This has been corroborated by the previously mentioned $^{13}$C- and methoxy $^1$H-NMR studies[1–9].




*VIA* H-1(*app*)$CH_3$
H-2($g^+g^-$)$CH_3$




*VIB* H-1(sc)$CH_3$
H-2($g^+a$)$CH_3$

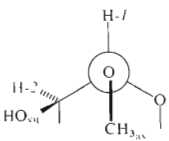



*VIC* H-1(sc)$CH_3$
H-2($g^+g^+$)$CH_3$

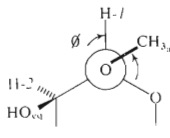
C—$OCH_3$ *Rotamers in methyl* β-D-*glucopyranoside*: With β-D-glucopyranose as the model compound the observed shift-displacements are −0·27(H-1) and +0·01

(H-2). Along the same lines of reasoning two interpretations may be given. Either *VIB* is the preponderant form, or an admixture with almost equal populations of *VIA* and *VIC* may be present. The latter possibility results from the fact that the effects on both H-1 and H-2 in *VIA* and *VIC* are opposite and may well cancel out each other. In view of the exo-anomeric effect[19] however, rotamer *VIB* should be the rotamer of our choice.

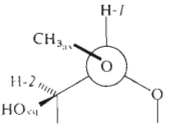
C—$OCH_3$ *Rotamers in methyl* α-D-*glucopyranoside*: The observed increments are −0·43(H-1) and +0·06(H-2), taking α-D-glucopyranose as the reference compound. Again *VIIA* is improbable (that would result in a downfield shift for H-1 but




*VIIA* H-1(*app*)$CH_3$
H-2(*ap*)$CH_3$




*VIIB* H-1(sc)$CH_3$
H-2(*aa*)$CH_3$




*VIIC* H-1(sc)$CH_3$
H-2(*ap*)$CH_3$

an upfield shift for H-2), and *VIIC* also is less likely because H-2 would suffer from an important downfield effect. In accordance with the presence of an *exo*-anomeric effect[19] rotamer *VIIB* is found to be the major form.

4-O-*Methyl*-β-L-*arabinopyranose*: β-L-Arabinopyranose occurs in the inverted chair form[20] with an axial 4-OH group. The extracted $^1$H-NMR data for the 4-$OCH_3$ derivative, together with those of pyranoses that we need for reference (α,β-L-arabinopyranose and β-D-xylopyranose) are collected in Table IV. The relevant increments found in the methylated arabinopyranoses with respect to the free pyranoses are; for the β-form: +0·04(H-3), −0·36(H-4), +0·18(H-5eq.) and −0·10(H-5ax). For the α-form they are very similar: +0·04(H-3), −0·35(H-4), +0·20(H-5eq.) and −0·14(H-5ax). The three rotamers which may cause these shifts are shown in *VIIIA*–*VIIIC*. Because of the important upfield effect on H-4, rotamer *VIIIA* may be neglected, as expected ($OCH_3$ pointing over the ring), as is also the case for *VIIIB*, because it would be hard to explain the position of H-3, H-5eq. and H-5ax for which the effects should be reversed. Only *VIIIC* is in agreement with the observations.

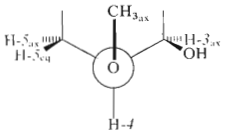
TABLE IV

Chemical Shifts and Coupling Constants of α,β-L-Arabinopyranose and 4-O-Methyl-α,β-L-arabinopyranose in $D_2O$ (TSP)

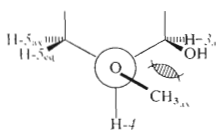
| Chemical shifts: | H-1 | H-2 | H-3 | H-4 | H-5eq | H-5ax |
|---|---|---|---|---|---|---|
| β-D-Xylopyranose[a] | 4·57 | 3·23 | 3·42 | 3·63 | 3·93 | 3·32 |
| α-L-Arabinopyranose[b] | 4·52 | 3·51 | 3·66 | 3·95 | 3·91 | 3·67\|+0·35\| |
| β-L-Arabinopyramose[b] | 5·24 | 3·82 | 3·89 | 4·01 | 3·66 | 4·01 |
| 4-O-Methyl-α-L-arabinopyranose[c] | 4·51(−0·01) | 3·45(−0·06) \|+0·22\| | 3·70(+0 04) \|+0·28\| | 3·60(−0·35) | 4·11(+0·20) \|+0·18\| | 3·53(−0·14) \|+0·21\| |
| 4-O-Methyl-β-L-arabinopyranose | 5·22(−0·02) | 3·76(−0·06) | 3·93(+0·04) | 3·65(−0·36) | 3·84(+0·18) | 3·91(−0·10) |

| Coupling constants: | $J$(1,2) | $J$(2,3) | $J$(3,4) | $J$(4,5e) | $J$(4,5a) | $J$(5e,5a) |
|---|---|---|---|---|---|---|
| β-D-Xylopyranose[a] | 7·8 | 9·2 | 9·0 | 5·4 | 10·5 | −11·4 |
| β-L-Arabinopyranose[b] | 7·8 | 9·7 | 3·7 | 2·3 | 1·0 | −12·6 |
| α-L-Arabinopyranose[b] | 3·4 | 9·8 | 3·2 | 2·5 | 1·6 | −12·6 |
| 4-O-Methyl-α-L-arabinopyranose | 7·8 | 9·8 | 3·6 | 2·0 | 1·0 | −13·4 |
| 4-O-Methyl-β-L-arabinopyranose | 3·7 | 9·9 | 3·6 | 2·4 | 1·4 | −13·1 |

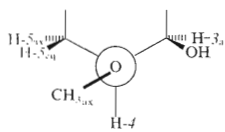
[a] From ref.[26]. [b] From ref.[20]. [c] Values between ( ) are increments *vs* β-L-arabinopyranose, those between | | *vs* β-D-xylopyranose.




*VIIIA* H-4(*app*)$CH_3$
H-3($ag^+$)$CH_3$
H-$5_{ax}$($ag^-$)$CH_3$
H-$5_{eq}$($g^-g^-$)$CH_3$

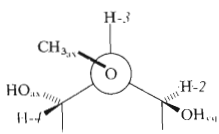



*VIIIB* H-4(sc)$CH_3$
H-3($ag^-$)$CH_3$
H-$5_{ax}$(*aa*)$CH_3$
H-$5_{eq}$($g^-a$)$CH_3$




*VIIIC* H-4(sc)$CH_3$
H-3(*aa*)$CH_3$
H-$5_{ax}$($ag^+$)$CH_3$
H-$5_{eq}$($ag^-$)$CH_3$

3-O-*Methyl*-β-D-*gulopyranose*: Table V gives the $^1$H-NMR data. The increments with respect to β-D-gulopyranose are +0·02(H-2), −0·40(H-3) and +0·21(H-4).




*IX* H-3(sc)$CH_3$
H-2(*aa*)$CH_3$
H-4($g^+g^-$)$CH_3$

TABLE V
300 MHz $^1$H-NMR Data of β-D-Gulopyranose and 3-O-Methyl-β-D-gulopyranose in $D_2O$

| Chemical shifts: | H-1 | H-2 | H-3 | H-4 | H-5 | H-6A | H-6B |
|---|---|---|---|---|---|---|---|
| β-D-Gulopyranose[a] | 4·88 | 3·63 | 4·07 | 3·82 | 4·00 | 3·75 | 3·74 |
| 3-O-Methyl-β-D-gulopyranose | 4·81 | 3·65 | 3·67 | 4·03 | 3·92 | 3·74 | 3·74 |
| Increment[b] | −0·07 | +0·02 | −0·40 | +0·21 | −0·08 | — | — |
| **Coupling constants:** | *J*(1,2) | *J*(2,3) | *J*(3,4) | *J*(4,5) | *J*(5,6A) | *J*(5,6B) | *J*(6A, 6B) |
| β-D-Gulopyranose[a] | 8·4 | 3·2 | 3·8 | 1·4 | 6·6 | 5·8 | — |
| 3-O-Methyl-β-D-gulopyranose | 8·0 | 3·5 | 3·5 | 1·2 | —[c] | —[c] | —[c] |

[a] From reference[24]; [b] *versus* β-D-gulopyranose; [c] Degenerated to a deceptively simple AA'X spin system.

TABLE VI
Increments of the C—O($CH_3$) Bond

| Compound | OR-group | Observed proton | Effect |
|---|---|---|---|
| Methyl α-D-glucopyranoside | C-1 | H-2 | *app* |
| Methyl α-D-glucopyranoside | C-1 | H-3 | synax |
| 4-O-Methyl-α-L-arabino-pyranose | C-4 | H-3 | *app* |
| 4-O-Methyl-α-L-arabino-pyranose | C-4 | H-2 | synax |

The rotamer *IX* is therefore the preponderant form in agreement with what was expected taking the foregoing cases into consideration.

*Cumulative effects*: *Methyl* 2-O-*methyl*-α *and* β-D-*glucopyranoside*: When we confront the increments found in the methyl 2-O-methyl-α,β-D-glucopyranosides with those encountered in the corresponding methyl α,β-D-glucopyranosides and the 2-O-$CH_3$-derivatives, it is found that the net increment-values are the sum-values (*e.g.* for the β-derivatives: experimental: −0·23(H-1), −0·25(H-2) and +0·09(H-3); sum values: −0·27(H-1), −0·28(H-2) and +0·17(H-3); and for the α-derivatives: experimental: −0·18(H-1), −0·21(H-2) and −0·02(H-3); sum values: −0·16(H-1), −0·18(H-2) and 0·0(H-3)). We therefore conclude that the individual rotameric populations of the methoxy substituents are not affected by each other.

*Effect of the* C—O($CH_3$) versus C—O(H) *bond* on *ring protons*: We have previously proposed refined Lemieux-Stevens increments for aldohexopyranoses[21] (taking β-D-glucopyranose as the reference) and for aldopentopyranoses[22] (taking β-D-xylopyranose as the reference). It was interesting to look for possible differences when a C—O(H) bond is changed into a C—O($CH_3$) bond, *e.g.* looking for any change in the proposed values that would result from contributions others* than arising from the additional O—$CH_3$ bond anisotropy and its relative spatial disposition. Table VI (values deduced after correction for the rotameric contribution) shows that the effects are similar for C—O($CH_3$) and C—O(H) bonds, *e.g.* +0·22 ± 0·07 ppm for an app

* Alternatively, these additional effects may arise from the O—$CH_3$ bond anisotropy on protons further remoted than for β- and γ-effects, see also δ-effects.

TABLE VI
(*Continued*)

| Correction | Positioning for corr. | Correction value | Exp. value | Increment |
|---|---|---|---|---|
| $OCH_3$ | $H(aa)CH_3$ | −0·02/−0·05 | +0·29 | +0·24/+0·27 |
| $OCH_3$ | — | — | +0·24 | +0·24 |
| $OCH_3$ | $H(aa)CH_3$ | −0·02/−0·05 | +0·28 | +0·23/+0·26 |
| $OCH_3$ | secondary effects | −0·06 | +0·29 | +0·23 |

TABLE VII
δ-Effects

| Compound | Proton | δ-Effect | Value |
|---|---|---|---|
| Methyl α-D-glucopyranoside | H-3 | $H(g^+g^-a)CH_3$ | −0·03 |
| | H-5 | $H(g^-g^+g^+)CH_3$ | −0·02 |
| 2-O-Methyl-α-D-glucopyranose | H-4 | $H(g^-g^+a)CH_3$ | −0·07 |
| 4-O-Methyl-α-L-arabinopyranose | H-2 | $H(g^-g^+a)CH_3$ | −0·06 |
| 4-O-Methyl-β-L-arabinopyranose | H-2 | $H(g^-g^+a)CH_3$ | −0·06 |
| 3-O-Methyl-β-D-gulopyranose | H-1 | $H(g^-g^+a)CH_3$ | −0·07 |
| | H-5 | $H(g^+g^-g^-)CH_3$ | −0·08 |

C—O($CH_3$) in aldohexopyranoses and +0·23 ± 0·03 ppm for a synaxial C—O($CH_3$) group. The increment of 4-$OCH_3$ in 4-O-methyl-α,β-L-arabinopyranoses on H-5ax is +0·21 ppm when compared to α,β-D-xylopyranoses. Hence, this value may be considered as arisen from a rotameric contribution (−0·10/−0·14 ppm) and one coming from the C(4) − O(4) bond, with a resultant value of +0·21 − (−0·10/−0·14) = = +0·31/+0·35 ppm. This is exactly the value observed in α-L-arabinopyranose *versus* the same reference compound β-D-xylopyranose. Therefore, the *app* effect of either an C—O(H) or C—O($CH_3$) on a proton which belongs to a methylene grouping (H-5 in aldopentopyranoses) is larger than when it belongs to a methine grouping. It is known that increments indeed are "substrate sensitive", and the same effect as

the present one has been observed in other hexacyclic compounds[15]. We find further that in methyl α-D-glucopyranoside the synaxial increment on H-5 amounts only to +0·25 ppm (ref.[23-25]), whereas a value of +0·40 ppm is normally found[21,22] for a *syn*-axial OH.

*δ-Effects*: In the previous examples, the rotameric distribution of an axial methoxy group seems to be well established. We have extracted therefore the δ-effects, characterised by the conformational fragments $H(g^-,g^+,a)CH_3$ and $H(g^+,g^-,g^-)CH_3$ (or the enantiomeric situations). There is a good indication that they cause a small upfield displacement of $-0{\cdot}05 \pm 0{\cdot}03$ ppm (Table VII).

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