Carbohydrate Research, 62 (1978) 19–26

ASSIGNMENT OF CONFIGURATION AT QUATERNARY CENTRES IN PAIRS OF 3-*C*-HYDROXYMETHYL AND 3-*C*-METHYL BRANCHED-CHAIN 1,2:4,6-DIACETALATED ALDOHEXOPYRANOSE DERIVATIVES USING ^{13}C-N.M.R. SPECTROSCOPY

PETER M. COLLINS AND V. RANJIT N. MUNASINGHE

Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX (Great Britain)

(Received April 25th, 1977; accepted for publication May 5th, 1977)

ABSTRACT

The configuration at the C-3 quaternary carbon atoms in two pairs (**1** and **2**, **3** and **4**) of 3-*C*-hydroxymethyl, branched-chain, 1,2:4,6-diacetalated aldohexopyranoses have been determined from their ^{13}C-n.m.r. spectra. The stereochemical assignments were achieved by comparison of the spectra with those of the *Z* (**13**) and *E* isomers (**14**) of 4-*tert*-butyl-1-hydroxymethylcyclohexanol and with those of the corresponding diacetalated gluco- and allo-pyranoses (**5**, **6**, **9**, and **10**). The spectra of **13** and **14** showed that an axial hydroxyl group shielded the α, β, and γ ring carbon atoms more than an axial hydroxymethyl group and that the carbon atom in the latter group was shielded relative to that in an equatorial hydroxymethyl group. The spectra of **5**, **6**, **9**, and **10** indicated the effect of an axial HO-3 on the shifts of the carbon atoms in the 1,2-*O*-alkylidene groups. The stereochemistry of an isomeric pair of 1,2:4,6-di-*O*-alkylidene-3-*C*-methyl-aldohexopyranoses (**11** and **12**) has also been determined.

INTRODUCTION

From a study[1] of the photoreactions of aldopyranos-3-ulose derivatives in methanol, pairs of 3-*C*-hydroxymethyl branched-chain sugar derivatives were obtained which required stereochemical assignments. Most of the methods employed for determining the configuration at the quaternary carbon atom in branched-chain[2] pyranoid derivatives containing the R-C̆-OH group measure changes in chemical or physical properties associated with the axial or equatorial orientations of the hydroxyl group[3]. Many of these methods are less reliable if R also contains a hydroxyl group.

^{13}C-N.m.r. spectroscopy has already been applied extensively to sugar derivatives, and correlations between structure and ^{13}C parameters have been established[4–6]. The method has also been applied successfully to pyranoses possessing 1,3-dithian-2-yl and methyl groups as branching substituents[7–9].

We now report on ^{13}C chemical shifts and configurational assignments for

TABLE I

^{13}C-CHEMICAL SHIFTS (P.P.M. FROM Me_4Si) FOR 1,2:4,6-DIACETALATED ALDOHEXOPYRANOSE DERIVATIVES IN $CDCl_3$ AT 15.0 MHz

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-3'*[a]	*C-7*	*C-8*	*Sub-7*		*Sub-8*
1	96.4	80.6	71.2[c]	84.9	60.9	69.8[d]	63.8[d]	104.8	102.1	27.0	8.1	
2	98.0	71.1	69.3[c]	76 9	59.4	69.3[d]	64.7[d]	102.7	102 0	26 8	8.3	126.3 ±0.1
5	98.3	77.2	73.7	79.7	63.1	68.7[d]	—	102.7	101.8	27.6	7.8	128.3 ±0.1
6	97.9	70.2	63.9	77.1	58.2	69.1[d]	—	102.7	102.1	26.6	8.3	129.2 ±0.1
7	97.7	77 2	81.1	80 3	62 1	69.1	(58 6)[b]	103.1	101.5	27.3	7.8	137.1 ±0 1
8	97.7	70.0		76.9	58.2	69.1	—	102.8	102.1	26.6	8.3	
3	96 2	79.9	70.8[c]	84 9	61.1	69 3[d]	63.8[d]	108 8	99.9	25.4	27.0	20.4
4	97.3	72.0	69.2[c]	76.6	58.2	68 8[d]	65.3[d]	108.2	99.8	26.4	26.4	20.4
9	98.0	78 0	73.7	79.1	63.0	68.4[d]	—	108.1	99.7	27 2	27.9	20.4
10	97.3	71.2	64.3	76.7	57.8	68.8[d]	—	108.4	100.2	26.2	26.7	20.5
11	96.8	81 1	71 8[c]	83 4	62 2	69.3[d]	20 2	108 3	99.9	25.7	27 0	20.4
12	97.5	76 4	67 5[c]	80.4	59.5	68.8[d]	25.5	108.2	100.2	26.4	26.4	20.4

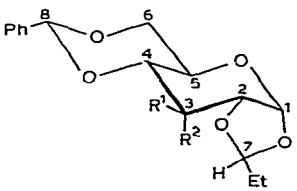
[a]Carbon atom in branched group attached to C-3. [b]MeO-3. [c]Singlet in SFORD spectrum. [d]Triplet in SFORD spectrum.

two isomeric pairs of 1,2.4,6-diacetalated pyranoid derivatives with C-3 hydroxymethyl branching-groups[1], and one pair with a C-3 methyl branch.

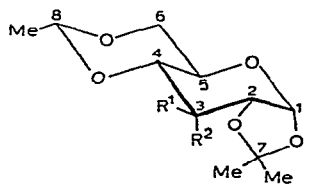
The ^{13}C chemical shifts are recorded in Table I, and the assignments have been made by applying the general rules[5] and those developed for sugars[4,6], and from off-resonance decoupled spectra.

RESULTS AND DISCUSSION

The 4,6-*O*-benzylidene-1,2-*O*-propylidene derivatives **1**, **2**, and **5–8** all exhibit four signals at low field (between 126.2 and 137.2 p.p.m.), due to the aromatic-ring carbon atoms of the benzylidene residue[8,10], and two signals at high field (8.05 ±0.25 and 27.1 ±0.5 p.p.m.), due to the ethyl groups of the propylidene residues. The 4,6-*O*-ethylidene-1,2-*O*-isopropylidene derivatives **3**, **4**, and **9–12** each gave two



1 R^1 = OH, R^2 = CH_2OH
2 R^1 = CH_2OH, R^2 = OH
5 R^1 = OH, R^2 = H
6 R^1 = H, R^2 = OH
7 R^1 = OMe, R^2 = H
8 R^1 = D, R^2 = OH



3 R^1 = OH, R^2 = CH_2OH
4 R^1 = CH_2OH, R^2 = OH
9 R^1 = OH, R^2 = H
10 R^1 = H, R^2 = OH
11 R^1 = OH, R^2 = Me
12 R^1 = Me, R^2 = OH

13 R^1 = CH_2OH, R^2 = OH
14 R^1 = OH, R^2 = CH_2OH
15 R^1 = CH_3, R^2 = OH
16 R^1 = OH, R^2 = CH_3

signals in the range 25.4–27.9 p.p.m., due to the isopropylidene methyl groups[7], and a signal at higher field, ~20.4 p.p.m., similar to the value reported for the methyl group in 2-methyl-1,3-dioxane[11]. Therefore, this signal must be due to the methyl group in the 4,6-*O*-ethylidene residue.

The C-7 and C-8 acetal carbon atoms in **1**–**12**, which are linked to either O-1 and O-2 or O-4 and O-6, should give signals at low field. In **1**, **2**, and **5**–**8**, C-8 of the *O*-benzylidene group resonates at 101.8 ±0.3 p.p.m., in agreement with reported values[7], whereas C-7 of the *O*-propylidene group resonates at lower field (102.7–104.8 p.p.m.). The acetal carbon in a dioxolane ring should resonate at lower field than one in a dioxane ring[6]. For the 4,6-*O*-ethylidene residue in **3**, **4**, and **9**–**12**, the resonance for C-8 appeared at 99.7–100.2 p.p.m., predictably less-deshielded than C-8 in the benzylidene analogues, whereas C-7 of the isopropylidene group in **3**, **4**, and **9**–**12** was 6.0 p.p.m. more deshielded than C-7 in the propylidene analogues, in keeping with a change from a quaternary to a tertiary carbon atom.

In the branched-chain sugar derivatives **1**–**4**, the C-1 resonances were readily identified as the lowest field signals which remained unassigned. The C-3 branching positions were identified from the off-resonance decoupled spectra, in which they remained diagnostically as singlets, and this technique also revealed the resonances for C-6 and C-3′ (the hydroxymethyl carbon atom) as triplets. The lower field signal of the two was assigned to C-6, because it was part of a dioxane ring and should be deshielded relative to the exocyclic C-3′ atom which carries a hydroxyl group[10]. Furthermore, the couplings between the two equivalent protons and C-3′ were cleanly decoupled, whereas those between the C-6 signal and H-6*eq* and H-6*ax* were not. This observation supports the proposed assignment[12].

Each of the three carbon atoms remaining unassigned was attached to one hydrogen atom and consequently not distinguishable in the off-resonance decoupled spectra. The signal at highest field, arising from these three atoms, could be assigned[7,10] to C-5, and the other two were assigned to either C-2 or C-4. The latter carbon is assumed to resonate at lower field for the same reasons that C-4 is more deshielded than C-2 in the hexopyranose derivatives **5**–**10** (see below).

The signals for the two *C*-methyl branched-chain sugar derivatives **11** and **12** were assigned by similar methods and by reference to literature values[7].

In the non-branched glucose and allose derivatives **5**, **6**, **9**, and **10**, all of the hexosyl carbon atoms, except C-3, were assigned by methods similar to those used for **1**–**4**. The signal for C-4 was distinguished from that of C-2 by reference to the signals for C-4 for other 4,6-acetalated derivatives of α-D-allosides and α-D-glucosides[7,10]. The C-3 atoms could not be distinguished by off-resonance decoupling, but since they were the only carbons carrying hydroxyl groups, they were allotted to the highest field resonance at 73.7 and 63.9 (or 64.3) p.p.m. in the spectra of **5** and **9**, and **6** and **10**, which remained unassigned after the resonances for C-5 and C-6 had been located. Confirmation of these assignments was obtained with the 3-*C*-deuterioallose derivative **8** and the 3-*O*-methylglucose derivative **7**. The spectrum of **8** was almost identical to that of the unlabelled analogue **6**, except that the signal

at 63.9 p.p.m. was absent[6,13]. All of the resonances, apart from that of C-3, in the spectrum of **7** were within 1.0 p.p.m. of those found for the unmethylated derivative **5**. However, the C-3 resonance (73.7 p.p.m.) in the spectrum of **5** was replaced by a signal at 81.1 p.p.m. in the spectrum of **7**. This shift is consistent with the known behaviour of carbinol carbon atoms upon *O*-methylation[13].

In conformationally locked cyclohexane derivatives, the effect of the orientation of a substituent on ^{13}C chemical shifts is well-documented[5]. These changes may be used to predict configurations at tertiary centres. The situation with geminally disubstituted cyclohexane derivatives is more subtle, as a substituent occupies an axial position in both configurations, and consequently the difference in chemical shifts for each isomer will probably be less marked than when one substituent is hydrogen.

The branched-chain sugars considered herein are mainly pyranose derivatives geminally substituted with hydroxyl and hydroxymethyl groups. Therefore, for comparison, the structurally less-complex *Z* (**13**) and *E* isomers (**14**) of 4-*tert*-butyl-1-hydroxymethylcyclohexanol were prepared[14]. The difference in ^{13}C chemical shifts of the α, β, γ, δ, and substituent carbon atoms in the two isomers are recorded in Table II. All of the carbon atoms of the cyclohexane ring, except the δ carbon (C-4), are shielded more by an axial hydroxyl group than by an axial hydroxymethyl group. As might be expected, the magnitude of these differences is smaller than those found with the isomers of 4-*tert*-butylcyclohexanol[15], but close to that found for the *Z* (**15**) and *E* isomers (**16**) of 4-*tert*-butyl-1-methylcyclohexanol[7]. Furthermore, the carbon atom of an axial hydroxymethyl substituent is shielded by 6.0 p.p.m. relative to that found for the isomer. This agrees closely with the findings[16] for the isomers of 4-*tert*-butyl-1-hydroxymethylcyclohexane. The carbon atoms of the methyl groups in **15** and **16** are also similarly affected.

Stereochemical assignments can therefore be made for the branched-chain sugar derivatives **1–4** by applying the results found for **13** and **14**. Compounds **2** and **4** may be assigned the *allo* configuration (axial HO-3) for the following reasons. The quaternary carbon atom (C-3) resonates 1.9 and 1.6 p.p.m. (see Table III) to higher field in these compounds than in their respective isomers **1** and **3**; the summa-

TABLE II

THE DIFFERENCE IN CHEMICAL SHIFTS FOR CORRESPONDING CARBON ATOMS IN (*Z*)- AND (*E*)-1-ALKYL-4-*tert*-BUTYLCYCLOHEXANOLS

HO-1 (ax) — (eq)	α *C-1*	β *2/6*	γ *3/5*	δ *C-4*	*C-1'*
13 — 14	−1.4	−1.2	−2.4	+0.7	+6.0
15 — 16[a]	−2.1	−1.6	−1.4	−0.1	+6.0

[a]Values taken from Ref. 7.

TABLE III

THE DIFFERENCE IN CHEMICAL SHIFTS FOR CORRESPONDING CARBON ATOMS IN C-3 BRANCHED-CHAIN 1,2:4,6-DIACETALATED PYRANOSE ISOMERS

HO-3 (ax) — (eq)	*γ* *C-1*	*β* *2/4*	*β* *4/2*	*α* *C-3*	*γ* *C-5*	*C-3'*
2 — 1	+1.6	−8.0	−9.9	−1.9	−1.5	+0.9
4 — 3	+1.1	−7.9	−8.3	−1.6	−2.3	+1.5
6 — 5[a]	+0.4	−7.0	−2.6	−9.8	−4.9	
12 — 11	+0.7	−4.7	−3.4	−4.3	−2.7	+5.3

[a]Non-branched derivatives included for comparison.

tions of the chemical shifts of the pyranose-ring carbon atoms, *i.e.*, ∑C-1,2,3,4,5 (see Table I), indicate[13,17] that these atoms are more shielded in **2** and **4** than in **1** and **3**. Also, the carbon atoms of the hydroxylmethyl groups resonate 0.9 and 1.5 p.p.m. to lower field in these compounds than in their respective isomers **1** and **3**, indicating that the hydroxymethyl group must be axial in the latter compounds.

Application of these criteria to the *C*-methyl branched-chain sugar derivatives **11** and **12**, and reference to the cyclohexane derivatives **16** and **15**, indicate that they possess the *gluco* and *allo* configurations, respectively.

The stereochemistry proposed above for the quaternary carbon atoms in the branched-chain sugar derivatives **1** and **2**, **3** and **4**, and **11** and **12** can be corroborated by comparing the chemical shifts of some of the nuclei of their 1,2-*O*-alkylidene residues with those in related glucose and allose derivatives. This is possible because the 1,2-*O*-alkylidene residues in the *allo* compounds are subject to the same steric interactions as those in the corresponding allose derivatives, whereas the steric effect in branched-chain *gluco* compounds would be different from those in glucose derivatives.

The chemical shifts of the two methyl carbons in the isopropylidene residue in **4** and **12** are within 0.3 p.p.m. of those in the allose derivative **10**, but they differ by as much as 1.5 p.p.m. from those in the glucose derivative **9**. This indicates that **4** and **12** have an axial hydroxyl group, as does **10**. In **3** and **11**, on the other hand, the shifts of these carbon atoms differ markedly from those in **10** and **9**, which indicates that **3** and **11** have the branching group axially disposed, and consequently have the *gluco* configuration.

The tertiary, acetal carbon atoms (C-7) of the isopropylidene groups in **3**, **4**, and **9**–**12** are all similar and therefore of little value for stereochemical assignment. However, in the 1,2-*O*-propylidene derivatives **1**, **2**, **5**, and **6**, it is the chemical shifts of these carbon atoms (C-7) which are of value for determining stereochemistry. In the branched-chain derivative **2**, C-7 resonates at the same value (102.7 p.p.m.) as that found in the allose derivative **6** and, coincidentally, the same as that found for the glucose derivative **5**, whereas C-7 resonates at 104.8 p.p.m. in the branched-

chain derivative **1**. This difference is consistent with a change in steric interaction anticipated from an axial hydroxymethyl group.

EXPERIMENTAL

The ^{13}C-n.m.r. spectra were obtained with a Jeol FX-60 system operating in the Fourier-transform mode. All compounds were examined as 5–10% solutions in $CDCl_3$ (internal Me_4Si). Carbon types, *i.e.*, methyl, methylene, methine, and quaternary, were identified by off-resonance decoupling.

The branched-chain sugar derivatives **1–4** were prepared photochemically[1], and **5** and **9** were prepared by condensation of D-glucose with the required aldehyde or ketone[1].

4,6-O-Benzylidene-1,2-O-propylidene-α-D-allopyranose (**6**) *and its 3-C-deuterio analogue* (**8**). — A solution of 4,6-*O*-benzylidene-1,2-*O*-propylidene-α-D-*ribo*-hexopyranos-3-ulose[1] (0.1 g) in ethanol (10 ml) and dichloromethane (5 ml) was reduced with sodium borohydride (0.1 g) at 20° during 2.5 h. The usual work-up gave **6** (80%) as needles, m.p. 126°, $[\alpha]_D^{21}$ +96° (*c* 2.6, chloroform). N.m.r. data ($CDCl_3$): δ 5.42 (d, $J_{1,2}$ 5.5 Hz), 4.05 (t, $J_{2,3}$ 5.5 Hz), 4.15–4.64 (H-3,4,5), 3.5–3.85 (H-6,6′), 2.66 (s, OH), 5.0 (t, H-7), 5.60 (s, PhC*H*), 1.66–2.04 (CH_2), 0.85–1.15 (t, *J* 7.5 Hz, Me), and 7.3–7.6 (Ph).

Anal. Calc. for $C_{16}H_{20}O_6$: C, 62.3; H, 6.5. Found: C, 62.3; H, 6.65.

Compound **8** was prepared as described above, but using sodium borodeuteride. The n.m.r. data were similar to those of **6**, except that the signal for H-3 was absent and that for H-2 was a doublet.

4,6-O-Benzylidene-3-O-methyl-1,2-O-propylidene-α-D-glucopyranose (**7**). — Compound **5** (0.1 g) was methylated by using benzene (10 ml) containing sodium hydride (0.2 g) and methyl iodide (1 ml). The usual work-up gave **7** (81%), m.p. 60°, $[\alpha]_D^{20}$ +40° (*c* 2.1, chloroform). N.m.r. data ($CDCl_3$): δ 5.54 (d, $J_{1,2}$ 5.0 Hz), 4.40 (dd, $J_{3,2}$ 4.0, $J_{3,4}$ 9.5 Hz), 3.5–4.1 (H-2,4,5,6,6′), 4.92 (t, *J* 4.5 Hz, H-7), 5.58 (s, PhC*H*), 3.56 (s, OMe), 1.6–1.9 (CH_2), 1.0 (t, *J* 7.2 Hz, Me), and 7.3–7.7 (Ph).

4,6-O-Ethylidene-1,2-O-isopropylidene-α-D-allopyranose (**10**). — Compound **10**, prepared from the corresponding 3-ulose by the method used for **6**, was obtained as needles (70%), m.p. 129°, $[\alpha]_D^{20}$ +123° (*c* 1.8, chloroform), ν_{max} 3510 cm^{-1} (HO), R_F 0.4 (ethyl acetate–dichloromethane, 1:4), *T* 5.2 min (215°). N.m.r. data: δ 5.56 (m, H-1, coupled to H-2,3), 4.1–4.4 (H-2,3,4,5), 3.3–3.6 (H-6,6′), 2.70 (s, OH), 4.80 (q, *J* 5.5 Hz, MeC*H*), 1.43 and 1.62 (2 s, CMe_2), and 1.39 (d, *J* 5.5 Hz, Me).

Anal. Calc. for $C_{11}H_{18}O_6$: C, 53.7; H, 7.4. Found: C, 53.9; H, 7.4.

4,6-O-Ethylidene-1,2-O-isopropylidene-3-C-methyl-α-D-glucopyranose (**11**). — 4,6-*O*-Ethylidene-1,2-*O*-isopropylidene-α-D-*ribo*-hexopyranos-3-ulose (0.25 g) was epoxidised with diazomethane, and the product was reduced with lithium aluminium hydride to give **11** as a syrup (71%), $[\alpha]_D^{20}$ + 35° (*c* 5.3, chloroform), *T* 16.0 min (10% SE-30, 10-ft column, 215°). N.m.r. data ($CDCl_3$): δ 5.66 (d, $J_{1,2}$ 4.5 Hz), 4.08 (d, $J_{2,1}$ 4.5 Hz), 3.47 (d, $J_{4,5}$ 10.0 Hz), 3.86 (td, $J_{5,6e}$ 5.0 Hz), 3.47 (t, $J_{6a,5}$ 10 Hz),

4.26 (dd, $J_{6e,6a}$ 10.0 Hz), 2.28 (broad s, OH), 1.57 (s, Me), 4.82 (q, *J* 5.0 Hz, MeC*H*), 1.36 (d, *J* 5.0 Hz, *M*eCH), 1.40 and 1.42 (2 s, CMe_2). Mass spectrum: *m/e* 260 (1%, M^+), 245 (9%, $M^+ - 15$), and 43 (100%).

4,6-O-Ethylidene-1,2-O-isopropylidene-3-C-methyl-α-D-allopyranose (**12**). — The foregoing 3-ulose derivative was treated with methylmagnesium bromide in the usual way, to give **12** (86%), m.p. 90°, $[\alpha]_D^{21}$ +101° (*c*, 3.8, chloroform). N.m.r. data ($CDCl_3$): δ 5.52 (d, $J_{1,2}$ 5.0 Hz), 3.86 (d, $J_{2,1}$ 5.0 Hz), 3.12 (d, $J_{4,5}$ 8.5 Hz), 4.0–4.35 (m, H-5,6e), 3.42 (t, $J_{6a,6e}$ 12.0, $J_{6a,5}$ 12.0 Hz), 1.60 (s, Me), 4.73 (q, *J* 5.0 Hz, MeC*H*), 1.40 and 1.32 (2 s, CMe_2), and 1.38 (d, *J* 5.0 Hz, *M*eCH). Mass spectrum: *m/e* 260 (1%, M^+), 245 (12%, $M^+ - 15$), and 43 (100%).

Z (**13**) *and* E *isomers* (**14**) *of* 4-tert-*butyl-1-hydroxymethylcyclohexanol.* — These compounds were prepared from 4-*tert*-butylcyclohexanone by the method of Whitham and Cross[14], but the mixture of diols, which had been partially purified by column chromatography, was converted into the *p*-nitrobenzoates, and the components were separated by p.l.c. on silica gel. Saponification of the more-mobile ester (R_F 0.87) gave the *E*-diol **14**, m.p. 125°; the other ester (R_F 0.63) gave the *Z*-diol **13**, m.p. 100°; lit.[14] m.p. 125° and 100°, respectively.

ACKNOWLEDGMENT

The authors thank Mr. R. Egan for the n.m.r. measurements.

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