Carbohydrate Research, 83 (1980) 3–7
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

^{13}C-N.M.R. SPECTRA OF METHYL 3,4-DIDEOXY-DL-GLYC-3-ENOPYRANOSIDES

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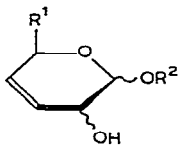
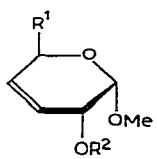
(Received May 29th, 1979; accepted for publication, October 19th, 1979)

ABSTRACT

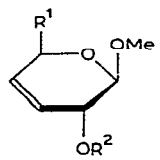
^{13}C-N.m.r., proton-decoupled spectra of 22 isomeric methyl 3,4-dideoxy-DL-glyc-3-enopyranosides are presented. Comparison of the data for compounds having HO-2 unsubstituted and acetylated enabled assignment of all of the resonances. Specific up- and down-field shifts made possible an unequivocal assignment of structure to 3,4-unsaturated methyl glycenopyranosides. On the basis of the chemical shifts of the signal for C-1, the position of the conformational equilibrium of methyl 3,4-dideoxy-DL-pent-3-enopyranosides could be estimated.



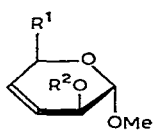
1 R^1 = H, Me, or CH_2OH ; R^2 = alkyl



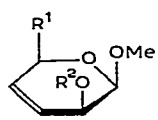
2 R^1 = R^2 = H
3 R^1 = H, R^2 = Ac
4 R^1 = $CEt(OMe)_2$, R^2 = H
5 R^1 = $CEt(OMe)_2$, R^2 = Ac
6 R^1 = CH_2OH, R^2 = H
7 R^1 = CH_2OAc, R^2 = Ac
8 R^1 = Me, R^2 = H
9 R^1 = Me, R^2 = Ac



10 R^1 = R^2 = H
11 R^1 = H, R^2 = Ac
12 R^1 = $CEt(OMe)_2$, R^2 = H
13 R^1 = $CEt(OMe)_2$, R^2 = Ac
14 R^1 = CH_2OH, R^2 = H
15 R^1 = CH_2OAc, R^2 = Ac



16 R^1 = CH_2OH, R^2 = H
17 R^1 = CH_2OAc, R^2 = Ac
18 R^1 = Me, R^2 = H
19 R^1 = Me, R^2 = Ac



20 R^1 = CH_2OH, R^2 = H
21 R^1 = CH_2OAc, R^2 = Ac
22 R^1 = Me, R^2 = H
23 R^1 = Me, R^2 = Ac

INTRODUCTION

The structure of alkyl 3,4-dideoxyglyc-3-enopyranosides (**1**) can usually be deduced from ^{1}H-n.m.r.[1-3] and m.s. data[4]. When the ^{1}H-n.m.r. spectra are too complex for interpretation[5] or when m.s. data are complicated by rearrangement processes (*e.g.*, double-bond migration occurring during fragmentation[4]), the assignment of structure may be difficult.

We have assessed the ^{13}C-n.m.r. spectra of a series of methyl 3,4-dideoxyglyc-3-enopyranosides in relation to their value for structure assignment.

Although ^{13}C-n.m.r. spectra for many carbohydrates have been recorded[6], data for unsaturated monosaccharides are scant, but have been reported for D-glycals[7] and some unsaturated precursors of methyl tobrosaminide[8].

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFTS FOR METHYL 3,4-DIDEOXY-DL-GLYC-3-ENOPYRANOSIDES **2–23**

Compound	*OMe*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	
2	55.99	98.14	64.21	126.94[a]	126.22[a]	59.95		
3	56.06	96.10	66.46	121.83	129.25	60.20		20.95, 170.56 Ac
4	56.21	98.57	64.34	127.39[a]	127.06[a]	68.37	102.39	8.57, 25.50 Et; 48.42, 48.92 2 OMe
5	56.18	96.33	66.89	122.35	129.51	68.50	102.42	8.58, 25.49 Et; 48.45, 48.96 2 OMe; 20.91, 170.50 Ac
6	56.04	98.23	64.36[a]	128.67	125.50	69.14	64.84[a]	
7	56.03	95.98	66.53[a]	124.34	127.90	66.82[a]	65.31	20.75, 20.87, 170.39, 170.62 2 Ac
8	55.97	98.32	64.27[a]	125.94	131.42	63.99[a]	20.65	
9	55.87	95.94	66.78	121.16	133.40	63.99	20.99	20.43, 170.40 Ac
10	55.98	102.23	64.78	124.81	128.48	60.70		
11	55.88	98.91	66.01	120.35	131.24	59.43		20.95, 170.12 Ac
12	56.40	104.56	67.51	128.68[a]	127.66[a]	75.62	102.25	8.46, 25.30 Et; 48.43, 49.02 2 OMe
13	56.04	101.39	69.11	124.54	130.50	75.38	102.13	8.44, 25.23 Et; 48.41, 49.05 2 OMe; 20.99, 170.10 Ac
14	56.67	103.78	66.83	128.60[a]	127.72[a]	75.50	64.92	
15	56.10	100.18	67.27	124.65	129.23	71.57	65.87	20.75, 20.95, 170.09, 170.64 2 Ac
16	55.97	101.82	63.48[a]	126.26	129.73	68.83	63.97[a]	
17	55.96	98.87	65.28[a]	122.37	130.82	66.26	65.39[a]	20.75, 20.92, 170.21, 170.62 2 Ac
18	55.94	101.63	64.03	123.76	134.26	64.03	20.34	
19	55.87	99.06	65.57	119.56	136.30	63.36	21.10	20.21, 170.30 Ac
20	56.50	100.11	63.48	127.67	129.48	75.25	64.46	
21	56.60	97.98	65.05[a]	124.23	129.96	71.76	65.76[a]	20.75, 20.92, 170.54, 170.62 2 Ac
22	56.14	100.09	63.58	125.35	134.09	70.34	21.17	
23	56.54	98.10	64.75	121.66	136.29	70.55	21.10	20.89, 170.62 Ac

[a]Assignments may be reversed.

RESULTS AND DISCUSSION

Fully proton-decoupled, ^{13}C-n.m.r. data for the derivatives **2–23** were obtained in the F.t. mode at 20 MHz and are recorded in Table I; all of the compounds were racemic, but, for convenience, D structures are depicted in the formulae. The signals for C-1 of the *erythro* compounds having HO-2 unsubstituted occurred at 98–98.5 p.p.m. for the α anomers and at 103–104 p.p.m. for the β anomers. This order is reversed in the *threo* series: α anomers, 101–102 p.p.m.; β anomers, 100 p.p.m. Each series displays the trend observed for many saturated hexopyranoses and alkyl hexopyranosides: α anomers with HO-2 equatorial have C-1 signals at higher field than do the β anomers. The reverse order is found for anomers of hexopyranoses having HO-2 axial.

^{1}H-N.m.r. data[3] for methyl 3,4-dideoxy-DL-hex-3-enopyranosides show that the substituent (Me or CH_2OH) at C-5 is pseudo-equatorial. Consequently, **4–9** and **12–23** occur preponderantly in the $^{0}H_{1}$ conformation, in which HO-2 (AcO-2) is pseudo-equatorial in the *erythro* series and pseudo-axial in the *threo* series.

The signals for C-2 occur in the narrow range 63.5–67 p.p.m. for both *erythro* and *threo* series and do not allow differentiation of configuration. The assignment of a signal to C-2 is sometimes complicated by the close proximity of signals for C-5 or C-6 (Table I; **6–8**, **16–18**, and **21**).

The signals for the olefinic carbon atoms appear in the range 120–136 p.p.m. The assignment of signals to C-3 and C-4 could be made after analysing the spectra of the 2-acetates (see below).

The chemical shift of the signal for C-4 depends on substitution at C-6. In methyl 3,4,6-trideoxyhex-3-enopyranosides, it appears at lower field (4.5–6 p.p.m.) in comparison with the corresponding signal of C-6-oxygenated compounds. This difference may be due to the gauche γ-substituent effect[9]. Also, the signal for C-3 is sensitive to the nature of the substituent at C-6 and is found at a higher field (2–2.5 p.p.m.) for 6-deoxy compounds compared to the corresponding signal for derivatives oxygenated at C-6.

Esterification causes[10] a downfield shift (2–4 p.p.m.) of the signal for the α-carbon atom of the original alcohol, and an upfield shift of that of the β-carbon atom. These changes were observed in the spectra of the acetates of the methyl 3,4-dideoxy-glyc-3-enopyranosides. The signals for C-2 were shifted downfield ~2 p.p.m., whereas those for C-1 appeared at 2–3 p.p.m. to higher field. The chemical shifts for the α, β, and γ carbon atoms of allylic alcohol[11] were 63.4, 137.5, and 114.9 p.p.m., respectively, and the corresponding signals for allyl acetate were 65.56, 132.73, and 118.19 p.p.m. Thus, acetylation shifted the signals of the α, β, and γ carbon atoms 2 p.p.m. downfield ~5 p.p.m. upfield, and ~3 p.p.m. downfield, respectively. Related upfield and downfield shifts were observed for the signals of C-3 and C-4 of the unsaturated methyl pyranosides on acetylation, and provide a basis for the assignment of the signals for these olefinic carbons.

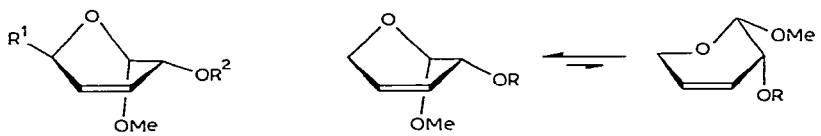
The chemical shifts of C-5 depend on the substituent (H, Me, or CH_2OH)

attached thereto and also on the configuration at C-1. For the α compounds (axial MeO-1) **4–9** and **16–19**, the signal for C-5 was shifted upfield 5–7 p.p.m. Acetylation of HO-6 led to an ~2 p.p.m. upfield shift of the signal for C-5.

The signals for C-6 appeared at 64–65 p.p.m. for the CH_2OH group and at 20–21 p.p.m. for the Me group. Acetylation of HO-6 shifted the signal for C-6 ~1 p.p.m. downfield.

The signals of the remaining carbon atoms, *i.e.*, OMe, Ac, and Et $(OMe)_2$, had typical chemical-shifts and showed no direct relation to the stereochemical features of the remainder of the molecules.

The data in Table I allow a semi-quantitative estimation of the conformational equilibria of the anomeric methyl 3,4-dideoxy-DL-pent-3-enopyranosides and their 2-acetates (**2**, **3**, **10**, **11**). The chemical shifts of the signals for C-1 of **2** and **3** closely resemble those of the corresponding signals for methyl 3,4-dideoxy-α-D-*erythro*-glyc-3-enopyranosides having HO-2 unsubstituted and acetylated (Table I; **4**, **6**, and **8**, and **5**, **7**, and **9**, respectively). For the latter, a distinct preference for the $^{\circ}H_1$ conformation was deduced[3] from ^{1}H-n.m.r. data. The same conformation follows therefore for **2** and **3**.



$^{\circ}H_1$ $^{\circ}H_1$ $^1H_0$

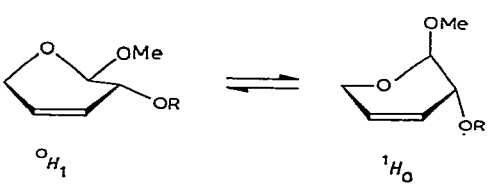
R^1 = Me, CH_2OH, CH_2OAc, $CEt(OMe)_2$

R^2 = H, Ac

2 R = H

3 R = Ac

If the average chemical-shifts (101.7 and 104.2 p.p.m., respectively) of C-1 for the α-*threo* compounds **16** and **18** and β-*erythro* compounds **12** and **14** are taken as the limiting values for the $^{\circ}H_1$ and $^1H_0$ conformations, then the chemical shift (102.2 p.p.m.) of C-1 for the β anomer **10** corresponds to ~77% of the $^1H_0$ conformation in the $^{\circ}H_1 \rightleftharpoons {}^1H_0$ equilibrium. Likewise, the 2-acetate **11** is concluded to be ~92% in the $^1H_0$ conformation, the increase reflecting the allylic effect after esterification.



$^{\circ}H_1$ $^1H_0$

10 R = H

11 R = Ac

These qualitative conclusions are similar to those derived from ^{1}H-n.m.r. data[3]. Thus, the ^{13}C-n.m.r. data for the methyl 3,4-dideoxy-glyc-3-enopyranosides and their esters permit an unequivocal assignment of constitution.

EXPERIMENTAL

Compounds **2**, **3**, **6–11**, and **14–23** were obtained as described earlier[6,7]; the syntheses of **4**, **5**, **12**, and **13** will be described elsewhere[12].

^{13}C-N.m.r. spectra at 20 MHz were recorded for 10% solutions in $CDCl_3$ (internal Me_4Si) at room temperature with a Varian CFT-20 spectrometer. Chemical shifts are given in p.p.m. downfield from the reference signal.

ACKNOWLEDGMENT

This work was supported by PAN grant MRI. 12.1.7.4.

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