CONFIGURATION AND CONFORMATION OF METHYL 2,3-ANHYDRO-4-DEOXY-PYRANOSIDES BY ^{1}H AND ^{13}C NMR SPECTRA

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Abstract—^{13}C NMR spectra of 24 methyl 2,3-anhydro-4-deoxy-pento and hexopyranosides have been obtained. ^{1}H NMR spectra were also recorded for comparison purposes. The ^{13}C NMR data can be used for differentiation of the stereo-isomeric epoxide configuration. ^{1}H and ^{13}C NMR spectra give some insight, though still of qualitative nature, into conformation of epoxy compounds.

Sugar epoxides (usually alkyl 2,3- or 3,4-anhydro-pyranosides) are valuable and widely used substrates (or intermediates) in chemical modifications of monosaccharides.[1,15] Although the basic rules governing the oxirane ring-opening reactions by nucleophiles are essentially the same as those established for simple cyclic epoxides,[2] the reactions of sugar epoxides are often dependent on a few additional factors. Some of these factors like the influence of the anomeric center, participations of neighbouring groups or possibility of epoxide migration are connected with the specific sugar structure.[2]

Bannard *et al.*[3] indicated an additional factor which can play a role in reactions of epoxides—steric hindrance exerted by the incoming nucleophile. Product like transition states (e.g. A and B) are assumed in order to visualize this effect:
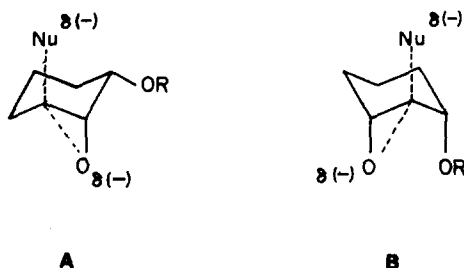
Transition state **A** is preferred over **B** exhibiting a 1,3-diaxial interaction; this explains the reason of the preferential attack of the nucleophile at C-3. There are examples in the carbohydrate field which demonstrate the usefulness of Bannard's concept of the direction of 3-membered ring opening.[4,5]

This concept stresses the importance of conformational effects in epoxide reactions. It is clear therefore

that knowledge of ground-state conformation of sugar epoxides is of interest.

Conformation of methyl 2,3- and 3,4-anhydro-pyranosides was studied earlier by means of ^{1}HNMR spectra.[6–9]

In recent years ^{13}C NMR spectra of epoxides have been investigated[10–14] and useful correlations connecting chemical shifts of epoxide C atoms with structural parameters have been proposed.[10,13,14] Until now, however, no information is available about ^{13}C NMR spectra of monosaccharide epoxides which occur in many stereoisomeric forms.

We have recorded ^{13}C NMR spectra of 24 "simplified" sugar epoxides: stereoisomeric methyl 2,3-anhydro-4-deoxy-pento- and hexopyranosides and have found that valuable conclusions regarding their configuration and conformation can be drawn. ^{1}H NMR spectra were also recorded for comparison purposes.
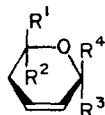
RESULTS

Methyl 2,3-anhydro-4-deoxy-pyranosides occur in half-chair forms.[15] Their unsaturated precursors: methyl 2,3,4-trideoxy-2-enopyranosides are conformationally similar; we decided therefore to compare ^{13}C and also ^{1}H NMR spectra of these two sets of compounds.

We recorded proton decoupled natural abundance [13]C Fourier transform and 100 MHz ^{1}H NMR spectra of unsaturated compounds 1–7 and stereoisomeric epoxides 8–31.†

Comparison of the spectra of structurally related compounds led us to the ^{13}C NMR signal assignments shown in Table 1.

DISCUSSION

It was previously reported[16] that differences in ^{13}C NMR chemical shifts of the C-2 and C-6 atoms can be employed for discrimination between *cis* and *trans* isomers of 2,6-disubstituted 5,6-dihydro-2H-pyrans as well as estimation of the conformational equilibrium. It was shown that *trans* isomers exist in $^{0}H_{5}$ conformation,‡ whereas in *cis* isomers the existence of both,

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†All investigated compounds were racemates. For simplification, formulae in this paper refer to compounds of D series: see also footnote on page 3326.

‡We are using the notation of conformation according Ref. 17.

1: $R^1 = R^2 = R^4 = H$, $R^3 = OMe$
2: $R^1 = CH_2OAc$, $R^2 = R^4 = H$, $R^3 = OMe$
3: $R^1 = CH_2OAc$, $R^2 = R^3 = H$, $R^4 = OMe$
4: $R^1 = CO_2tBu$, $R^2 = R^4 = H$, $R^3 = OMe$
5: $R^1 = CO_2tBu$, $R^2 = R^3 = H$, $R^4 = OMe$
6: $R^1 = R^2 = CO_2Et$, $R^3 = OMe$, $R^4 = H$
7: $R^1 = R^2 = CH_2OAc$, $R^3 = OMe$, $R^4 = H$
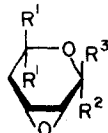
8: $R^1 = R^3 = H$, $R^2 = OMe$
9: $R^1 = R^2 = H$, $R^3 = OMe$
10: $R^1 = CO_2Et$, $R^2 = OMe$, $R^3 = H$
11: $R^1 = CO_2Et$, $R^2 = H$, $R^3 = OMe$
12: $R^1 = CH_2OAc$, $R^2 = OMe$, $R^3 = H$
13: $R^1 = CH_2OAc$, $R^2 = H$, $R^3 = OMe$
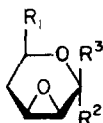
14: $R^1 = CH_2NHAc$, $R^2 = OMe$, $R^3 = H$
15: $R^1 = CH_2OAc$, $R^2 = OMe$, $R^3 = H$
16: $R^1 = CONH_2$, $R^2 = OMe$, $R^3 = H$
17: $R^1 = CO_2Bu$, $R^2 = OMe$, $R^3 = H$
18: $R^1 = CO_2tBu$, $R^2 = OMe$, $R^3 = H$
19: $R^1 = CONH_2$, $R^2 = OEt$, $R^3 = H$
20: $R^1 = CH_2NHAc$, $R^2 = H$, $R^3 = OMe$
21: $R^1 = CH_2OAc$, $R^2 = H$, $R^3 = OMe$
22: $R^1 = CONH_2$, $R^2 = H$, $R^3 = OMe$
23: $R^1 = CO_2tBu$, $R^2 = H$, $R^3 = OMe$
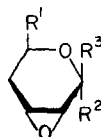
24: $R^1 = CH_2NHAc$, $R^2 = OMe$, $R^3 = H$
25: $R^1 = CH_2OAc$, $R^2 = OMe$, $R^3 = H$
26: $R^1 = CONH_2$, $R^2 = OMe$, $R^3 = H$
27: $R^1 = CO_2Bu$, $R^2 = OMe$, $R^3 = H$
28: $R^1 = CO_2tBu$, $R^2 = OMe$, $R^3 = H$
29: $R^1 = CN$, $R^2 = OMe$, $R^3 = H$
30: $R^1 = CH_2OAc$, $R^2 = H$, $R^3 = OMe$
31: $R^1 = CO_2tBu$, $R^2 = H$, $R^3 = OMe$
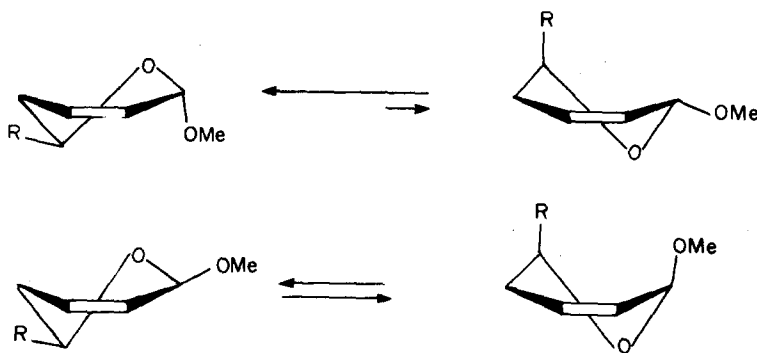
$R = H$, CO_2tBu, CH_2OAc

Scheme 1.

i.e. $^0H_5$ and $^5H_0$, conformers must be taken into account (Scheme 1).

Position of the equilibrium was estimated earlier on the basis of ^1H NMR spectra; it was found to be dependent on the type of substituent at the C-6 atom.[18,19]

After epoxidation the 6-membered ring remains in the halfchair form. For mobile systems the preferred conformation is that in which the substituent at C-5 is in equatorial orientation.[20] However, the nature of this substituent as well as other factors like anomeric effect, Reeves effect, etc. play an important role in establishing the conformational equilibrium. It can be deduced from ^1H and ^{13}C NMR spectra that methyl 2,3,4-trideoxy-pent-

‡Strictly speaking this compound should be named according to nomenclature of heterocyclic compounds as 2-methoxy-5,6-dihydro-2H-pyran. However, we prefer in this paper sugar nomenclature for all compounds because: (i) it assures uniform numbering of atoms in dihydropyran and sugar compounds and (ii) conformational and configurational designations are more convenient.

2-enopyranoside (1)‡ prefers $^0H_5$ form with pseudoaxial OMe group[16,18,19] (Scheme 1, R = H). Upon epoxidation of 1 two anhydro compounds, 8 and 9, are formed.[21] Due to the anomeric effect both epoxides 8 and 9 prefer this conformation in which the OMe group adopts pseudoaxial orientation, i.e. $^0H_5$ for 8, and $^5H_0$ for 9 (see Table 2 and Scheme 2).

One can arrive at a similar conclusion by analyzing the ^{13}C NMR chemical shift of the acetal C atom. The values δ 95.57 ppm for 8, and 96.75 ppm for 9 strongly support the preferred conformations. Probably for 9 a small contribution of the alternative form should be taken into account. The signal of the C-5 atom in the spectra of 8 and 9 is shifted upfield by 2.4 and 3.3 ppm, respectively, in comparison with that of unsaturated compound 1. An upfield shift could be expected on the basis of the ^{13}C NMR studies of steroidal epoxides[3] and epoxycyclohexane.[10] If the γ-C atom bearing an axial hydrogen is opposed by the epoxide O atom a strong shielding effect is exerted on the range of 3.5–6.0 ppm. Although such an

Table 1. ^{13}C NMR chemical shift of methyl 2,3,4-trideoxy-pent-and hex-2-enopyranosides (1–7) and methyl 4-deoxy-2,3-anhydropento and hexopyranosides (8–31)

N°	OCH₃	C-1	C-2	C-3	C-4	C-5	C-6	C-6'	
1[a]	55.1	95.4	129.3	126.7	25.5	57.7			
2[a]	55.1	95.6	128.3	126.6	27.1	65.4	66.8		171.1 (C=O), 20.7 (CH₃)
3[a]	55.1	97.0	127.9	127.7	26.7	69.8	66.4		171.1 (C=O), 20.7 (CH₃)
4	55.49	95.97	127.74	125.58	27.52	66.16	170.27		81.46, (–C≡) 28.09 (CH₃)
5	55.42	97.37	127.84	126.57	27.97	70.27	170.30		81.25 (–C≡), 26.42 (CH₃)
6	55.96	96.17	126.09	124.38	28.43	76.52	168.18	168.63	61.60 (CH₂), 61.84 (CH₂'), 13.86 (CH₃), 14.05 (CH₃')
7	55.39	95.17	125.23	125.16	26.91	71.86	63.65	66.63	170.26 (C=O), 170.64 (C=O'), 20.75, (CH₃)
8	55.29[b]	95.57	51.02	49.64	24.93	55.22[b]			
9	55.41	96.75	49.83	49.68	23.81	54.41			
10	56.28	96.17	49.44	49.35	28.17	78.51	167.66	168.24	61.94 (CH₂), 62.39 (CH₂'), 13.97 (CH₃)
11	56.93	97.14	49.10	48.31	28.56	75.32	168.19	168.43	62.00 (CH₂), 61.85 (CH₂'), 13.85 (CH₃), 14.02 (CH₃')
12	55.80	96.75	50.10	49.60	26.74	73.53	65.38	66.40	170.06 (C=O), 170.41 (C=O'), 20.74 (CH₃)
13	56.22	96.51	49.04	47.59	26.15	70.97	65.26	66.41	170.0 (C=O), 20.63 (CH₃)
14	55.55	96.53	49.55	49.03	25.89	62.96	42.92		170.14 (C=O), 25.12 (CH₃)
15	55.10	96.30	49.30	48.79	25.21	62.21	65.73		170.37 (C=O), 20.53 (CH₃)
16	56.06	96.86	49.53	48.93	26.17	64.16	173.49		
17	55.5	96.5	49.1	48.9	26.1	63.8	170.5		64.7, 30.8, 19.4, 13.7 (Bu)
18	56.00	96.7	49.5	49.2	26.4	64.5	169.8		82.4 (–C≡), 28.5 (CH₃)
19	—	95.54	49.54	49.17	26.21	64.09	174.55		64.58 (CH₂), 15.06 (CH₃)
20	56.49	99.16	50.85	49.89	25.46	71.63	42.95		173.09 (C=O), 23.33 (CH₃)
21	56.40	98.66	50.55	49.82	25.04	70.49	65.80		170.81 (C=O), 20.76 (CH₃)
22	56.91	98.88	50.64	49.85	25.67	72.38	173.34		
23	55.9	99.3	50.3	49.9	26.3	72.8	170.5		81.7 (–C≡), 28.3 (CH₃)
24	55.02	95.65	50.80	50.57	28.12	64.04	43.10		170.41 (C=O), 22.87 (CH₃)
25	54.81	95.61	50.75	50.21	27.01	62.97	66.14		170.34 (C=O), 20.49 (CH₃)
26	55.78	96.03	50.74	50.56	28.15	65.04	173.16		
27	55.6	96.2	51.4	50.5	28.8	64.6	170.9		65.0, 31.3, 19.8, 13.2 (Bu)
28	55.4	96.3	51.0	50.3	28.7	65.2	170.3		81.2 (–C≡), 28.3 (CH₃)
29	54.83	95.89	50.48	49.22	29.24	56.16	117.75		
30	56.09	98.80	52.85	50.42	26.94	65.09	66.09		70.33 (C=O), 20.52 (CH₃)
31	56.50	99.40	52.1	50.2	27.7	67.1	170.3		81.7 (–C≡), 28.2 (CH₃)

[a] Data taken from Ref. 16.
[b] Assignments may be reversed.
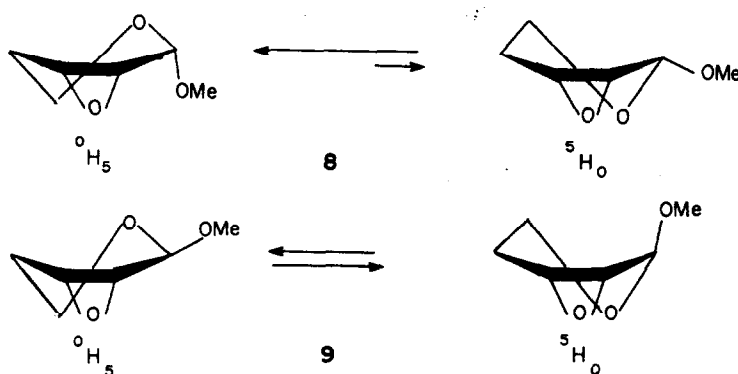
Scheme 2.

arrangement is encountered in the preferred conformation of 8, the numerical value of the upfield shift is rather low, especially, if one realizes that the C-5 atom is also opposed by the pseudoaxial OMe group. The upfield shift of C-5 in 9 can be only interpreted by the OMe group opposition in ^5H_o conformation.

Introduction of a substituent at C-5 of the 2,3-an-

hydropyranoside ring stabilises—according to ^{1}H NMR data (see Table 2)—$^oH_5$ conformation of compounds 14–31 (Scheme 3). Only for β-lyxo epoxides 20–23 some contribution of ^5H_o half-chair, or alternatively, some deformation of $^oH_5$ conformation must be taken into account.

^{13}C NMR spectra of α- and β-lyxo epoxides (Table 1)
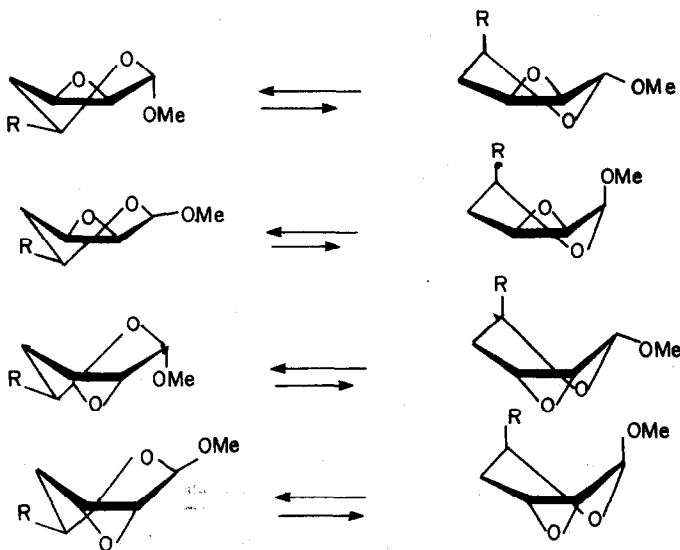
Scheme 3.

14, 20, 15, 21, 16, 22, and **18, 23** show that signals of the C-5 atom in α anomers are shifted upfield by about 8.3 ppm. This difference in chemical shift is associated with an axial shielding effect of the OMe group. The steric γ-effect of the epoxide ring is reflected in the ^{13}C NMR chemical shift changes of the C-5 atom when passing from β-lyxo to β-ribo epoxides, this upfield shift amounts to 5.4 ppm for **30** and 5.7 ppm for **31**. It is interesting to note that γ-shielding effects of the pseudoaxial OMe group and the epoxide ring are not additive. This is evident when one compares the C-5 chemical shift of α-ribo epoxides **24–29** with that of other related diastereoisomers. It is certainly not possible to explain low values of γ-effect of epoxides **24–29** in terms of conformational equilibrium.

^{13}C NMR spectra of compounds **14–31** allow also the configurational assignment. The chemical shift of the C-4 atom is influenced by the configuration of the epoxide. The signal appears at δ 25.0–26.4 ppm for α- and β-lyxo epoxides and at 27.0–29.0 ppm for both ribo epoxides. Thus the C-4 in combination with the C-1 signal can be used for differentiation of all stereoisomeric methyl 2,3-anhydro-4-deoxy-hexopyranosides.

In the case of ribo compounds, the pyranose ring oxygen and the epoxide O atom are *trans* positioned with regard to C-3, C-4, C-5 plane (arrangement A on Scheme 4). In the lyxo epoxides both O atoms are *cis* positioned forming array **B** (Scheme 4). We assume that the upfield shift of the resonance signal of C-4 atom in lyxo epoxides is due to the shielding effect of arrangement **B** relative to A.

A   **B**
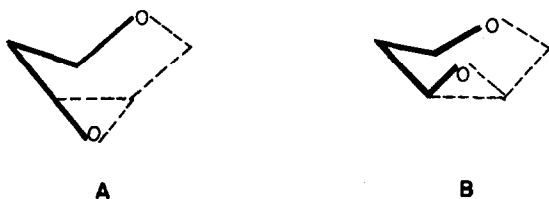
Upon introduction of two substituents at the C-5 atom of hex-2-enopyranose ring the position of conformational equilibrium is changed significantly (Scheme 5).
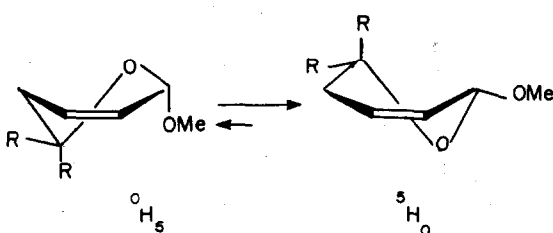

6: R = CO₂Et
7: R = CH₂OAc

Scheme 5.

The shift of equilibrium towards the [5]H₀ form is the result of the steric 1,3-effect of the axial substituent at C-5 and the pseudoaxial OMe group in the [0]H₅ conformer. It is difficult to estimate the position of actual equilibrium, however, ^{1}H NMR data (Table 2), e.g. chemical shifts of the OMe group, the value of homoallylic coupling constant[22] point at the participation of both half-chair conformations with distinct predominance of [5]H₀ form.

Epoxidation of unsaturated compounds **6** and **7** led to two pairs of stereoisomeric epoxides **10, 11** and **12, 13,** respectively. On the basis of ^{1}H NMR data (especially the magnitude of $J_{1,2}$) α-erythro configuration was assigned to **10** and to **12**.

Vicinal proton-proton coupling constants $J_{1,2}$, $J_{3,4}$ and $J_{3,4'}$, amount to 2.6, 1.6 and 2.3 Hz for **10**, and 2.0, 1.8 and 2.5 Hz for **12**, respectively (Table 2). These values strongly suggest that roughly equal proportions of both conformers participate in equilibrium (Scheme 6). This conclusion is particularly supported by the $J_{1,2}$ value which is smaller than in other related epoxides (e.g. **8, 24–29**) occuring preferentially in [0]H₅ conformation. On the other hand $J_{3,4}$ value (i.e. coupling constant between *cis* related protons) is close to zero, whereas for [5]H₀ conformation it should be in the range of 5 Hz.

Vicinal coupling constants of β-erythro epoxides ($J_{1,2} = 0$ Hz, $J_{3,4} = 4.2$ Hz and $J_{3,4'} = 1.5$ Hz for **11**, and $J_{1,2} = 0$ Hz and $J_{3,4+3,4'} = 5.8$ Hz for **13**) suggest the domination of [5]H₀ conformation in both cases.

^{13}C NMR data (Table 1) of epoxides **10–13** leads to similar conclusion. Due to the γ-effect of the axial

10: R = CO$_2$Et
12: R = CH$_2$OAc

11: R = CO$_2$Et
13: R = CH$_2$OAc
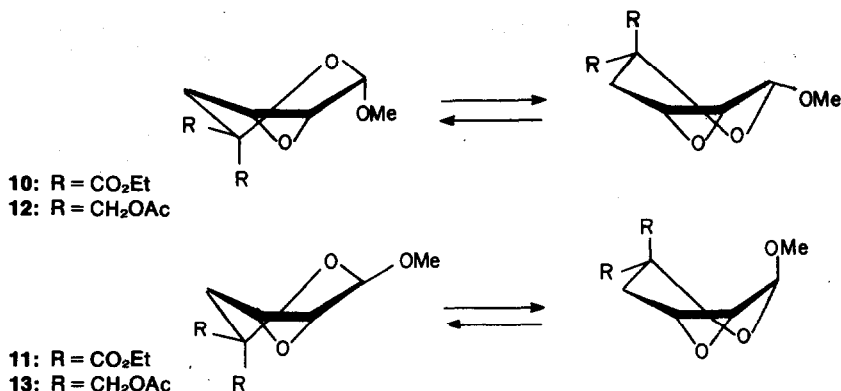
Scheme 6.

Table 2. ^{1}H NMR chemical shift and coupling constants of methyl 2,3,4-trideoxy-pent- and hex-2-enopyranosides (1, 6, 7) and methyl 4-deoxy-2,3-anhydro-pento and hexopyranosides (8–31)

	H-1	H-2	H-3	H-4	H-4'	H-5	OCH$_3$	
1	4.78	5.76	5.98	1.4——2.6		3.7	3.40	H–1 w/2 = 5.5 Hz
6	5.06	5.67	6.04	2.33	2.90		3.47	H–1 w/2 = 5.3 Hz, $J_{2,3}$ = 10.3, $J_{1,4eq}$ = 2 Hz
7	4.86	5.96	5.89	1.9——2.4			3.44	H–1 w/2 = 5.1 Hz
8	4.85	3.35		1.98		3.78	3.47	$J_{1,2}$ = 2.8 Hz
9	4.78	3.05	3.34	1.98		3.69	3.47	$J_{1,2}$ = 0, $J_{2,3}$ = 4.1 Hz
10	5.10	3.28	3.46	2.26	2.87		3.60	$J_{1,2}$ = 2.0, $J_{2,3}$ = 4.2, $J_{3,4}$ = 2.5 $J_{3,4'}$ = 1.8, $J_{4,4'}$ = 15.3 Hz
11	5.10	3.07	3.5	2.31	2.72		3.55	$J_{1,2}$ = 0, $J_{2,3}$ = 4.3, $J_{3,4}$ = 1.5, $J_{3,4'}$ = 4.2, $J_{4,4'}$ = 15.0 Hz
12	5.01	3.39		1.86	2.14		3.51	$J_{1,2}$ = 2.6, $J_{3,4}$ = 2.3, $J_{3,4'}$ = 1.6. $J_{4,4'}$ = 15.05 Hz
13	4.90	3.10	3.36	2.0			3.50	$J_{1,2}$ = 0, $J_{2,3}$ = 4.2, $J_{3,4}$ + $J_{3,4'}$ = 5.8 Hz
14	4.84	2.96		1.8——1.9		3.81	3.41	$J_{1,2}$ = 0, $J_{2,3}$ = 3.8 Hz
15	4.90	2.99	3.36	1.89		3.94	3.46	$J_{1,2}$ = 0, $J_{2,3}$ = 4.0 Hz
16	4.94	3.00	3.39	1.98	2.38	4.16	3.48	$J_{1,2}$ = 0, $J_{2,3}$ = 4.0, $J_{3,4}$ = 0, $J_{4,5}$ = 11.5, $J_{3,4'}$ = 5.7, $J_{4',5}$ = 5.0, $J_{4,4'}$ = 15.3 Hz
17	4.95	2.93	3.30	1.98	2.22	4.35	3.42	$J_{1,2}$ = 0, $J_{2,3}$ = 4.0, $J_{3,4}$ = 2.0 $J_{3,4'}$ = 1.5, $J_{4,4'}$ = 14.5, $J_{4,5}$ = 11.5, $J_{4',5}$ = 3.0 Hz
18[a]	5.12	3.05	3.43	2.1——2.3		4.27	3.57	$J_{1,2}$ = 0, ΣJ_5 = 16.5 Hz
20	4.76						3.57	$J_{1,2}$ = 0 Hz
21	4.80	3.14	3.39	1.89		3.77	3.56	$J_{1,2}$ = 0, $J_{2,3}$ = 4.2 Hz
22[a]	4.89	3.20		2.1——2.4		4.03	3.53	$J_{1,2}$ = 0, $J_{2,3}$ = 4.1, ΣJ_5 = 15.2 Hz
23[a]	4.94	3.21	3.45	2.1——2.4		4.06	3.66	$J_{1,2}$ = 0, $J_{4,5}$ = 8.8 $J_{4',5}$ = 6.0 Hz
24	4.93			1.67		3.83	3.44	$J_{1,2}$ = 3.0 Hz
25	4.95	3.35		1.5——2.2		3.99	3.44	$J_{1,2}$ = 3.2 Hz
26	5.00	3.31	3.4	1.80	2.54	4.24	3.46	$J_{1,2}$ = 3.3, $J_{2,3}$ = 4.2, $J_{3,4}$ = 1.4, $J_{4,4'}$ = 14.7, $J_{4,5}$ = 11.8, $J_{3,4'}$ = 1.9, $J_{4',5}$ = 3.0 Hz
27	5.00	3.22	3.38	1.39	1.82	4.32	3.41	$J_{1,2}$ = 3.0, $J_{2,3}$ = 4.0, $J_{3,4}$ = 2.0, $J_{3,4'}$ = 1.5, $J_{4,4'}$ = 14.5, $J_{4,5}$ = 11.5, $J_{4',5}$ = 3.0 Hz
28[a]	5.05	3.28	3.46	1.90	2.32	4.27	3.48	$J_{1,2}$ = 2.8, $J_{4,5}$ = 12.0 $J_{4',5}$ = 3.0 Hz
29	4.97	3.35	3.46	2.07——2.50		4.66	3.51	$J_{1,2}$ = 3.0, $J_{2,3}$ = 4.4, $J_{4,5}$ = 4.6, $J_{4',5}$ = 10.0 Hz
30	4.72	3.13	3.38	1.87		3.70	3.55	$J_{1,2}$ = 0, $J_{2,3}$ = 4.2, $J_{3,4}$ = 1.3, $J_{4,5}$ = 10.0, $J_{4,4'}$ = 14.7 Hz
31[a]	4.79	3.15	3.42	2.09	2.32	4.00	3.60	$J_{1,2}$ = 0, $J_{2,3}$ = 4.0, $J_{3,4}$ = 2.0, $J_{3,4'}$ = 2.0, $J_{4',5}$ = 4.5, $J_{4,4'}$ = 14.6, $J_{4,5}$ = 10.0 Hz

[a] Data taken from Ref. 4.

substituent at C-5 an upfield shift of the C-1 signal should be expected for conformers with a pseudoequatorial OMe group compared with that of the alternative form with a pseudoaxial OMe group. The signal of C-1 atom is shifted downfield in 11 and 13 compared with the appropriate signal of 10 and 12, this proves the greater contribution of $^{\circ}H_5$ form in the former two epoxides than in the latter.

The position of the C-4 signal in both anomeric pairs 10–11 and 12–13 is certainly more dependent on the type of substituent at C-5 than on anomeric configuration.

CONCLUSION

^{1}H NMR spectra don't allow an easy identification of stereoisomeric methyl 2,3-anhydro-4-deoxy-hexopyranosides. For ascertaining the isomer involved other data are usually required, i.e. chemical evidence (e.g. opening of the oxirane ring with an alcohol or amine) or tlc data (e.g. β-lyxo epoxides display usually small R_f values).

^{13}C NMR data make the identification of any stereoisomer of methyl 2,3-anhydro-4-deoxy-hexopyranoside easy. The C-1 signal determines the anomeric configuration and the C-4 signal delineates between the lyxo and ribo configuration of the epoxy ring.

^{1}H and ^{13}C NMR spectra give some insight, though still of a qualitative nature, into the conformation of epoxy compounds. At the actual stage of development the conclusions drawn from ^{1}H NMR data seem to be more reliable. Certainly further accumulation of ^{13}C NMR data is necessary in order to make the discussion of conformational relations more realistic.

EXPERIMENTAL

^{13}C NMR spectra were recorded in CDCl$_3$ on a Varian CFT-20 spectrometer at 20 MHz, with TMS as the internal standard; chemical shifts are given in ppm downfield from TMS.

^{1}H NMR spectra were recorded in CDCl$_3$ with a Joel JNM-4H-100 spectrometer operating at 100 MHz; δ scale, TMS = 0 ppm. Compounds 1–6 were obtained as described earlier.[4,23,24] Compound 7 was obtained by treatment of 6 with LAH in THF under standard conditions.

Epoxides 8–31 were obtained by epoxidation of their unsaturated precursors by means of m-chloroperbenzoic acid in chloroform soln according to the procedures described earlier.[4,20,21,25]

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