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THE ^{13}C NMR SPECTRA OF SOME *ENT*-18-HYDROXYKAUR-16-ENES

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Abstract—The ^{13}C NMR spectra are reported for thirteen *ent*-18-hydroxykaur-16-enes and their value for determining the C-4 stereochemistry is discussed.

The ^{13}C NMR spectra of a number of kauranoid diterpenoids have been assigned [1, 2] and the results have been applied in structural work. Although 19-oxygenation is probably the most common feature of the tetracyclic diterpenoids, a significant number of compounds occur, particularly in *Sideritis* (Labiatae) species [3–5], with a C-18 oxygen function. In the past the distinction between 18- and 19-oxygenation has involved, *inter alia*, ^{1}H NMR methods [6]. In connection with studies on microbiological transformations, we have assigned the ^{13}C NMR spectra of a group of 18-hydroxylated kauranoid diterpenes [7]. The results, which are given in Table 1, provide a useful distinction between these oxygenation patterns.

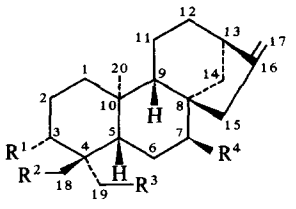
The resonances were assigned by conventional noise-decoupled and SFORD techniques and by comparison with the previous assignments [1]. Some 3-hydroxylated derivatives were included in the series since an oxygen function at this centre is both common and likely to affect the C-18 and C-19 resonances.

As expected the C-4 resonance is deshielded whilst the equatorial C-18 $\underline{C}H_2OH$ signal is at lower field than the axial C-19 $\underline{C}H_2OH$ (71.8 ppm vs 65.4 ppm). However the position may be modified by the presence of other substituents such as a C-3 hydroxyl group. The γ-gauche shielding effect of substituents has been used for stereochemical assignments on a cyclohexane ring [8]. The position of the resonances for C-3, C-5, C-18 and C-19

Table 1. ^{13}C NMR spectral signals of *ent*-18-hydroxykaur-16-enes in ppm from TMS

Carbon atom*	1	2	3	4	5	6†	7	8	9	10†	11	12	13
1	41.3	39.9	39.9	40.5	38.6	39.0	39.5	39.6	39.9‡	39.0	39.0	37.8	37.5‡
2	18.7	18.0	17.4	18.3	26.8	18.6	17.6	17.8	28.2	28.1	28.0	23.0	22.9
3	42.0	35.3	35.9	35.6	76.3	36.1	35.5	35.3	78.1	74.0	71.5	73.8	73.7
4	33.3	37.6	36.5	38.7	41.9	37.6	36.1	37.1	39.4	39.3	39.0	40.3	40.7
5	56.1	49.3	50.2	56.8	49.7	40.4	41.7	40.5	55.4	42.1	41.9	39.6	42.1
6	20.3	20.0	20.2	20.5	20.1	28.2	24.8	27.4	20.4	27.6	27.7	24.2	37.9‡
7	40.4	39.9	39.9	41.6	39.8	76.6	79.3	77.0	39.1	76.5	76.0	79.2	213.8
8	44.2	44.2	44.1	44.2	44.0	49.0	46.8	48.1	44.2	48.7	48.8	46.7	56.8
9	56.1	56.0	56.0	56.2	55.9	50.8	51.2	50.4	55.9	50.6	50.7	50.9	55.5
10	39.3	39.2	39.2	39.2	39.0	39.3	38.9	39.0	39.4	39.0	39.0	38.6	38.5
11	18.1	18.2	18.2	18.2	18.3	18.1	17.6	17.8	18.5	18.2	18.2	17.7	17.8
12	33.3	33.3	33.3	33.2	33.2	34.0	33.2	33.6	33.4	33.9	33.9	33.2	32.4
13	44.2	44.0	44.0	44.0	44.0	44.4	43.6	43.7	44.3	44.2	44.3	43.5	44.9
14	39.9	40.9	40.8	39.7	40.9	40.4	38.2	38.2	41.4‡	38.8	38.5	38.1	36.3
15	49.2	49.3	49.2	49.1	49.1	46.4	45.1	45.2	49.3	46.1	46.2	44.9	42.2
16	156.0	155.8	155.6	155.8	155.6	156.2	154.1	155.1	155.9	155.9	156.0	153.9	153.7
17	102.8	103.0	103.0	103.0	103.1	103.4	103.7	103.4	103.5	103.4	103.4	103.9	104.9
18	33.7	72.1	73.1	27.1	71.5	71.8	72.4	56.5	28.9	68.7	66.0	64.8	64.5
19	21.7	17.5‡	17.9	65.4	11.5	17.8	17.3	18.9	16.4	12.8	12.9	12.8	12.5
20	17.6	18.2‡	18.0	18.5	18.2	18.1	17.8	17.8	17.8	18.2	18.2	18.0	16.8

* Acetates: 20.8–21.1 and 170.3–171.1 ppm.
† In pyridine-d_5.
‡ These assignments may be interchanged.



1 $R^1 = R^2 = R^3 = R^4 = H$
2 $R^1 = R^3 = R^4 = H$, $R^2 = OH$
3 $R^1 = R^3 = R^4 = H$, $R^2 = OAc$
4 $R^1 = R^2 = R^4 = H$, $R^3 = OH$
5 $R^1 = R^2 = OH$, $R^3 = R^4 = H$
6 $R^1 = R^3 = H$, $R^2 = R^4 = OH$
7 $R^1 = R^3 = H$, $R^2 = R^4 = OAc$
8 $R^1 = R^3 = H$, $R^2 = Cl$, $R^4 = OH$
9 $R^1 = OH$, $R^2 = R^3 = R^4 = H$
10 $R^1 = R^2 = R^4 = OH$, $R^3 = H$
11 $R^1 = R^4 = OH$, $R^2 = OAc$, $R^3 = H$
12 $R^1 = R^2 = R^4 = OAc$, $R^3 = H$
13 $R^1 = R^2 = OAc$, $R^3 = H$, $R^4 = =O$

clearly shows the γ-gauche shielding effects by the hydroxyl substituents on C-3, C-18 and C-19 and hence provides a useful means of locating hydroxyl groups at these centres in new compounds. The effects of a C-3 and a C-18 hydroxyl group on C-19 are approximately additive. A hydroxyl group at C-7 also shows a γ-gauche shielding effect at C-5. An interesting contrast exists between the effect of an 18-hydroxyl and a 19-hydroxyl group on C-5. Only the former shows a γ-gauche effect on both C-3 and C-5 possibly reflecting the different conformations of the 18- and 19-hydroxyl groups.

A previous assignment of compound **6** (as its C-7 monoacetate) has been made independently [9]. Although our data are in general agreement, in the previous work [9] a signal at 24.3 ppm was assigned to C-2. An explanation for the difference ($\Delta\delta$ + 5.6 ppm) from *ent*-kaur-16-ene was proposed in terms of a conformational distortion of ring A. In our series we have assigned a signal at 18.0 ppm to C-2 (when there is no C-3 oxygen function) and hence there is no need to invoke a special conformational argument. A possible source of confusion is that these signals overlap with those for C-6 (24.3 ppm) or C-11 (17.7 ppm).

We conclude that ^{13}C NMR spectroscopy may assist in determining the stereochemistry at C-4 in these diterpenoids provided the shielding (or deshielding) effects of other neighbouring hydroxyl groups are also taken into account.

EXPERIMENTAL

The ^{13}C NMR spectra were determined at 20 or 25.15 MHz with $CDCl_3$ solns, except where stated. The isolation of the samples has been described previously [3–5, 7].

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