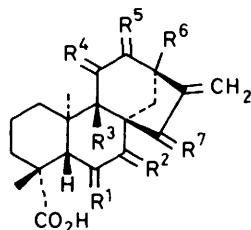


Carbon-13 Nuclear Magnetic Resonance Spectra of Eighteen Derivatives of *ent*-Kaur-16-en-19-oic Acid

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The ^{13}C n.m.r. spectra of eighteen derivatives of *ent*-kaur-16-en-19-oic acid are recorded and the additivity of substituent effects is investigated. Application of these additive effects to the prediction of the ^{13}C -shifts in new polysubstituted derivatives is assessed.

Several studies of the ^{13}C n.m.r. spectra of *ent*-kaurenoic (kaur-16-enoic) acids and kaurenolides have been reported and the identification of new substituted *ent*-kaurenoic acids has been achieved by a combination of ^1H - and ^{13}C -n.m.r. spectroscopy.¹⁻⁷ This paper concerns the ^{13}C n.m.r. spectra of the hydroxylated *ent*-kaurenoic acids (1), (2), (4)–(20).



	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷
(1)	H ₂	H ₂	H	H ₂	H ₂	H	H ₂
(2)	α -OH, H	H ₂	H	H ₂	H ₂	H	H ₂
(3)	β -OH, H	H ₂	H	H ₂	H ₂	H	H ₂
(4)	O	H ₂	H	H ₂	H ₂	H	H ₂
(5)	H ₂	α -OH, H	H	H ₂	H ₂	H	H ₂
(6)	H ₂	β -OH, H	H	H ₂	H ₂	H	H ₂
(7)	H ₂	O	H	H ₂	H ₂	H	H ₂
(8)	H ₂	H ₂	OH	H ₂	H ₂	H	H ₂
(9)	H ₂	H ₂	H	α -OH, H	H ₂	H	H ₂
(10)	H ₂	H ₂	H	H ₂	α -OH, H	H	H ₂
(11)	H ₂	H ₂	H	H ₂	β -OH, H	H	H ₂
(12)	H ₂	H ₂	H	H ₂	H ₂	OH	H ₂
(13)	H ₂	H ₂	H	H ₂	H ₂	H	α -OH, H
(14)	H ₂	H ₂	H	H ₂	H ₂	H	β -OH, H
(15)	H ₂	H ₂	H	H ₂	H ₂	H	O
(16)	β -OH, H	β -OH, H	H	H ₂	H ₂	H	H ₂
(17)	H ₂	β -OH, H	H	H ₂	H ₂	OH	H ₂
(18)	H ₂	β -OH, H	H	H ₂	H ₂	H	β -OH, H
(19)	H ₂	H ₂	H	H ₂	H ₂	OH	α -OH, H

Assignments.—The chemical shifts were assigned to individual carbon atoms from their multiplicities, by comparison with literature spectra, and by applying the substituent effects noted for simple acyclic and alicyclic alcohols and ketones.⁸⁻¹⁰ An additional aid was the availability of [15-,17-,19-,20- $^{13}\text{C}_4$]-labelled *ent*-7 α -hydroxy- and *ent*-6 α ,7 α -dihydroxy-kaurenoic acids (6) and (16), obtained from the incubation of potassium [3'- ^{13}C]mevalonate (24) with a cell-free system from the endosperm of *Cucurbita maxima*.¹¹ Where assignments remained equivocal, the carbons concerned were assigned on the assumption that changes in their chemical shifts with respect to the parent acid were minimal.

Results

The chemical shifts and their assignments are shown in Table 1 for deuteriochloroform solutions and in Table 2 for per-

deuteriopyridine solutions. The spectral data for the parent compound *ent*-kaurenoic acid (1) in deuteriopyridine (Table 2) are taken from the literature.⁵

Solvent effects are generally small. The most pronounced effect in the spectra of the *ent*-kaurenoic acids is at C-19 which is usually shielded, typically by 4–5 p.p.m., in perdeuteriopyridine relative to its shift in deuteriochloroform.

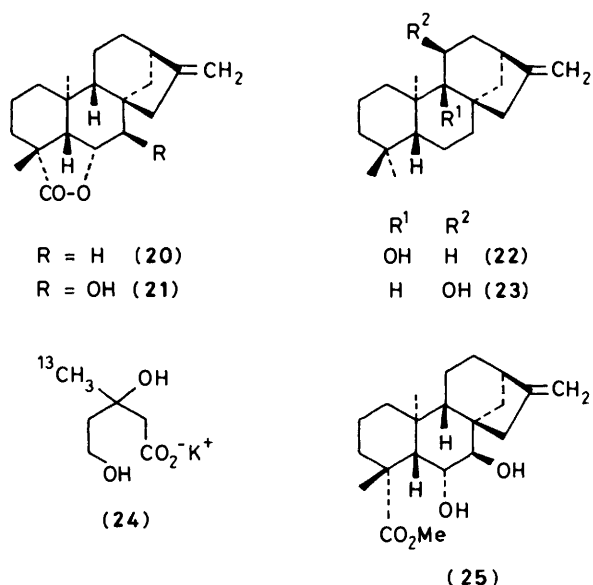
As illustrated below the shieldings/deshieldings caused by the proximity of the substituent to other carbons can be used to distinguish between epimers. Such effects are well known in the cholestane series, for example.^{12,13}

Discussion

In the spectrum of *ent*-6 β -hydroxykaurenoic acid (2), C-6 shows the expected large (*ca.* 35 p.p.m.) downfield shift, compared with its position in the spectrum of *ent*-kaurenoic acid (1). This large deshielding is characteristic of hydroxylation and is seen in the spectrum of each hydroxylated derivative except (8) where the downfield shift of C-9 is unusually small (22 p.p.m.). This is in contrast to the behaviour of steviol (12), the other compound containing a hydroxylated tertiary centre, and is attributed to diaxial interaction between the *ent*-9 α -hydroxy group and the *ent*-5 α - and *ent*-7 α -hydrogen atoms in compound (8). No such effect can be observed for the 13-hydroxy acid (12) since the hydroxy group is at a pseudo-equatorial position. The small deshielding of C-14, -19, and -20 upon *ent*-6 β -hydroxylation of *ent*-kaurenoic acid (1) may be attributed to the through-space proximity of the hydroxy function.

Lactonisation of the *ent*-6 β -alcohol and 19-oic acid functions in (2) to give kaurenolide (20) significantly affects the chemical shifts of many carbons. Those *sp*³ carbons remote from the newly formed γ -lactone are generally shielded by the transformation, whereas C-6 and -7 and all *sp*² carbons become deshielded. These data appear to support Hanson's report¹⁴ of a change in the B-ring conformation from that of a chair to a twist-boat upon lactonisation, and are also reasonably consistent with the literature data for *ent*-7 α -hydroxykaurenolide (21)² and methyl *ent*-6 β ,7 α -dihydroxykaurenoate (25)³ which bear almost the same relationship to one another. The effect of conformational change upon chemical shifts is also apparent in *ent*-7 α ,15 α -dihydroxykaurenoic acid (18) as discussed below, and suggests that ^{13}C n.m.r. spectroscopy may be more useful than ^1H n.m.r. for the study of these tetracyclic diterpenes. In the ^1H n.m.r. spectra, most protons merge into a methylene envelope, whereas in the ^{13}C n.m.r. spectra every carbon is normally separately resolved.

The 7-, 12-, and 15-hydroxy acids (5), (6), (10), (11), (13), and (14) have spectra which illustrate the effect of hydroxy group stereochemistry upon chemical shift. In all these cases, the change in chemical shift at the position of hydroxylation relative to the parent acid (1) does not directly reflect the stereochemistry, since the difference between epimers is small (0.5–



2.0 p.p.m.). In contrast, the change in chemical shift of any proton-bearing γ -carbons (*i.e.* carbon atoms two C-C bonds remote from the position of hydroxylation) is more indicative of hydroxylation stereochemistry. Thus, ' γ -*gauche*' interactions between hydroxy substituents and C $_{\gamma}$ protons cause a substantial (7–10 p.p.m.) shielding of γ -carbons, where ' γ -*trans*' interactions cause relatively minor shieldings. This is illustrated particularly well in the case of the 7- and the 15-hydroxylated derivatives where 7,15 (*gauche*) interactions cause shielding of the 15- (but not the 14-) carbon in the *ent*-7 α -hydroxy acid (6), and cause shielding of the 7- (but not the 14-) carbon in the *ent*-15 β -hydroxy acid (13). Conversely, C-14 is shielded (when compared with *ent*-kaurenoic acid) in the *ent*-7 β -alcohol (5), although the effect appears to be not so great in the *ent*-15 α -alcohol (14).

The effects upon C-9 of stereochemistry at the 7- and 15-

position are likewise dependent upon *gauche/trans* geometry, and C-9 is shielded predominantly in the *ent*-7 α - and *ent*-15 α -alcohol (6) and (14). Conversely, both C-7 and -15 are shielded by 9-hydroxylation. Effects upon neighbouring carbon atoms are approximately equal in both 12-epimers (10) and (11), but C-14 is shielded only in the *ent*-12 β -hydroxy acid (10) compared with its position in the spectrum of the parent acid (1). Interestingly, in the *ent*-12 β - (but not the *ent*-12 α -) alcohol (10), C-20 is relatively shielded (by *ca.* 1.3 p.p.m.), presumably due to its through-space proximity to the hydroxy group. A similar but opposite effect may be seen in the spectrum of the *ent*-11 β -hydroxy acid (9), where both C-1 and -20 become deshielded relative to their positions in that of *ent*-kaurenoic acid. In the spectrum of the 9-hydroxykaurenoic acid (8) also, C-20 is deshielded relative to its position in that of the parent acid (1); but C-1 is now shielded (by the γ -*gauche* interaction *via* the 1-protons). These observations are in good agreement with those recently reported⁷ for the corresponding *ent*-9 α - and *ent*-11 α -hydroxylated kaurenes (22) and (23).

C-13, -12, and -14 suffer the expected deshielding upon 13-hydroxylation of *ent*-kaurenoic acid as seen in the spectrum of steviol (12). In contrast, the *sp*² carbons C-16 and -17 are not deshielded by the 13-hydroxy function. Interestingly, shielding of both C-9 and -15 (1–2 p.p.m.) is observed in deuteriochloroform, and is somewhat greater than that in perdeuterio-pyridine solution.

The spectra of the three ketones investigated show the usual large deshielding of the carbonyl carbon. For the 6- and 7-oxo acids (4) and (7), the expected large deshieldings of the β -carbon atoms are apparent. In contrast, the ketone group at C-15 in *ent*-15-oxokaurenoic acid (15) forms part of an α,β -unsaturated system with the result that C-16 is shielded and C-17 is deshielded, relative to their positions in the spectrum of the parent acid (1).

The through-space shielding of the carboxylic C-19 by the 6-ketone is the largest reported in any substituted kaurenoic acid. A 7-ketone shields C-15 although it has little effect on C-14. The 15-ketone reciprocates by shielding C-7, but only shields C-14 to a small extent. Interestingly, a 15-ketone also appears to be

Table 1. ¹³C N.m.r. spectra of kaurenoic acid derivatives in CDCl₃; δ values all relative to internal SiMe₄

Carbon	Compound									
	(1)	(4)	(20)	(7)	(8)	(9)	(12)	(13)	(14)	(15)
1	40.7 (CH ₂) ^d	41.4 (CH ₂) ^d	37.4 (CH ₂) ^d	40.5 (CH ₂) ^d	40.5 (CH ₂) ^d	42.1 (CH ₂) ^d	40.5	40.7 (t) ^e	40.6 (t) ^e	39.9 (t) ^e
2	19.1 (CH ₂)	18.7 (CH ₂)	17.6 (CH ₂)	18.9 (CH ₂)	19.1 (CH ₂)	19.1 (CH ₂)	19.0	19.1 (t)	19.2 (t)	18.8 (t)
3	37.8 (CH ₂)	38.5 (CH ₂)	28.8 (CH ₂)	38.9 (CH ₂)	37.7 (CH ₂)	37.8 (CH ₂)	37.8	37.8 (t)	38.0 (t)	37.6 (t)
4	43.8	48.0	41.6	43.9	43.8	45.9	43.6	43.7 (s)	43.7 (s)	43.7 (s)
5	57.1 (CH)	67.1 (CH)	51.8 (CH)	54.9 (CH) ^a	50.1 (CH)	58.0 (CH)	56.9	57.0 (d)	56.4 (d)	56.0 (d)
6	21.8 (CH ₂)	219.3	75.4 (CH)	37.6 (CH ₂)	21.8 (CH ₂)	21.7 (CH ₂)	21.8	20.9 (t)	21.6 (t)	20.0 (t)
7	41.3 (CH ₂)	55.1 (CH ₂)	52.2 (CH ₂)	213.0	32.2 (CH ₂) ^a	42.2 (CH ₂) ^a	41.2	36.2 (t)	38.9 (t)	32.3 (t) ^a
8	44.2	50.7	39.9	57.8	44.0	41.1	41.8	47.7 (s)	45.7 (s)	52.5 (s)
9	55.1 (CH)	54.7 (CH)	53.5 (CH)	54.3 (CH) ^a	77.5 ^c	59.3 (CH)	53.8	53.3 (d)	45.5 (d)	51.6 (d)
10	39.7 ^b	43.5	34.5	39.6	49.2	39.5 ^b	39.5	39.8 (s)	39.3 (s)	40.3 (s)
11	18.4 (CH ₂)	18.5 (CH ₂)	16.8 (CH ₂)	17.9 (CH ₂)	29.5 (CH ₂)	70.8 (CH)	20.5	18.3 (t)	18.3 (t)	18.4 (t)
12	33.1 (CH ₂)	32.2 (CH ₂)	32.8 (CH ₂)	32.6 (CH ₂)	34.3 (CH ₂) ^a	42.7 (CH ₂) ^a	39.5	32.5 (t)	33.1 (t)	33.6 (t) ^a
13	43.9 (CH)	43.2 (CH)	38.1 (CH)	42.8 (CH)	42.2 (CH)	43.0 (CH)	80.4	42.3 (d)	40.0 (d)	38.1 (d)
14	39.7 (CH ₂)	39.5 (CH ₂)	35.8 (CH ₂)	38.9 (CH ₂)	36.1 (CH ₂) ^a	39.5 (CH ₂)	47.4 ^a	35.2 (t)	36.3 (t)	36.5 (t)
15	49.0 (CH ₂)	48.5 (CH ₂)	38.5 (CH ₂)	40.5 (CH ₂)	43.8 (CH ₂)	48.2 (CH ₂)	47.0 ^a	82.7 (d)	82.5 (d)	210.7 (s)
16	155.9	152.8	159.7	153.4	155.2	155.0	155.7	160.1 (s)	158.3 (s)	149.5 (s)
17	103.0 (CH ₂)	104.8 (CH ₂)	106.6 (CH ₂)	104.5 (CH ₂)	103.1 (CH ₂)	103.4 (CH ₂)	103.0	108.4 (t)	104.8 (t)	114.5 (t)
18	29.0 (CH ₃)	27.4 (CH ₃)	25.7 (CH ₃)	28.4 (CH ₃)	28.9 (CH ₃)	29.4 (CH ₃)	28.8	28.9 (q)	29.0 (q)	28.9 (q)
19	184.6	175.9	182.4	183.5	178.3	183.8	183.5	184.2 (s)	183.1 (s)	184.4 (s)
20	15.6 (CH ₃)	16.8 (CH ₃)	19.4 (CH ₃)	15.1 (CH ₃)	17.3 (CH ₃)	16.4 (CH ₃)	15.4	15.8 (q)	15.7 (q)	15.6 (q)

^a Signals may be interchanged within each column. ^b Signals not observed; inferred by comparison with spectrum of (1) in [2H₅]pyridine. ^c Position determined in CH₂Cl₂; obscured in CDCl₃. ^d Assigned by d.e.p.t. ^e Assigned by off-resonance decoupling.

Table 2. ^{13}C N.m.r. spectra of kaurenoic acid derivatives in $[\text{2H}_5]\text{pyridine}$

Carbon	Compound																			
	(1) ^s	(2) ⁱ	(20) ⁱ	(5) ⁱ	(6) ⁱ	(7) ⁱ	(10) ^c	(11) ^c	(12)	(13) ^c	(14) ^c	(15) ^c	(16) ^c	(17) ^c	(18) ^c	(19) ^c				
1	41.1	43.2 (CH ₂) ^e	37.5 (CH ₂) ^e	41.0 (t) ^f	40.9 (t) ^f	40.8 (CH ₂) ^e	41.4 (t) ^f	41.0 ^a	41.0 (t) ^f	41.2 (t) ^f	41.1 (t) ^f	40.3 (t) ^f	41.2 (t) ^f	41.0 (CH ₂) ^e	41.0 (t) ^f	41.1 (t) ^f				
2	19.8	20.1 (CH ₂) ^e	17.9 (CH ₂) ^e	19.9 (t)	19.7 (t)	19.6 (CH ₂) ^e	19.8 (t)	19.9	19.8 (t)	19.9 (t)	19.9 (t)	19.6 (t)	19.8 (t)	19.9 (CH ₂) ^e	19.9 (t)	19.8 (t)				
3	38.6	40.4 (CH ₂) ^e	29.2 (CH ₂) ^e	38.6 (t)	38.5 (t)	39.1 (CH ₂) ^e	38.7 (t)	38.7	38.6 (t)	38.8 (t)	38.7 (t)	38.5 (t)	39.0 (t)	38.8 (CH ₂) ^e	38.7 (t)	38.7 (t)				
4	43.8	42.5	41.8	43.7 (s)	43.7 (s)	43.2	44.0 (s) ^a	43.9 ^b	43.8 (s)	43.9 (s)	43.9 (s)	43.8 (s)	46.2 (s)	43.5	43.5 (s)	<i>d</i>				
5	57.1	66.3 (CH)	51.6 (CH)	54.8 (d) ^a	49.5 (d)	55.0 (CH) ^a	57.0 (d) ^b	56.8 ^c	57.0 (d)	57.2 (d)	56.7 (d)	56.3 (d)	52.0 (d)	48.7 (CH)	47.1 (d)	57.2 (d)				
6	22.5	57.4 (CH)	75.4 (CH)	32.3 (t) ^b	30.4 (t)	39.1 (CH ₂) ^e	22.6 (t)	22.6	22.6 (t)	22.1 (t)	22.4 (t)	20.8 (t)	71.8 (d)	30.7 (CH ₂) ^e	30.6 (t)	22.1 (t)				
7	41.5	46.8 (CH ₂) ^e	52.1 (CH ₂) ^e	74.7 (d)	76.2 (d)	212.1	41.7 (t)	40.6 ^a	41.9 (t)	36.7 (t) ^a	39.6 (t)	32.5 (t) ^a	81.9 (d)	76.3 (CH)	78.0 (d)	36.3 (t)				
8	44.4	46.2	40.0	50.8 (s)	48.9 (s)	58.0	43.9 (s) ^a	44.1 ^b	41.8 (s)	48.3 (s)	46.3 (s)	52.7 (s)	49.0 (s)	46.3	48.3 (s)	46.5 (s)				
9	55.2	55.3 (CH)	53.7 (CH)	54.1 (d) ^a	47.4 (d)	54.3 (CH) ^a	56.9 (d) ^b	56.4 ^c	54.2 (d)	54.0 (d)	46.0 (d)	52.0 (d)	49.2 (d)	47.4 (CH)	42.1 (d)	53.2 (d)				
10	39.9	39.6	34.7	40.1 (s)	39.5 (s)	39.9	39.1 (s)	39.1	39.8 (s)	40.2 (s)	39.6 (s)	40.6 (s)	41.2 (s)	39.7	39.4 (s)	40.1 (s)				
11	18.6	18.9 (CH ₂) ^e	17.0 (CH ₂) ^e	18.7 (t)	18.5 (t)	18.1 (CH ₂) ^e	26.7 (t)	29.4	20.7 (t)	18.7 (t)	18.4 (t)	18.7 (t)	18.4 (t)	20.6 (CH ₂) ^e	18.0 (t)	20.5 (t)				
12	33.3	33.4 (CH ₂) ^e	33.1 (CH ₂) ^e	34.0 (t)	34.0 (t)	32.8 (CH ₂) ^e	71.5 (d)	71.2	40.7 (t)	33.1 (t)	33.9 (t)	34.3 (t) ^a	33.9 (t)	41.4 (CH ₂) ^e	34.4 (t)	40.6 (t)				
13	44.2	44.8 (CH)	38.6 (CH)	43.9 (d)	44.3 (d)	43.2 (CH)	52.8 (d)	52.1	79.8 (s)	42.8 (d)	40.6 (d)	38.4 (d)	46.2 (d)	79.9	41.0 (d)	78.9 (s)				
14	39.9	41.9 (CH ₂) ^e	36.1 (CH ₂) ^e	31.6 (t) ^b	39.1 (t)	39.7 (CH ₂) ^e	33.8 (t)	39.5	47.4 (t) ^a	36.4 (t) ^a	36.8 (t)	36.7 (t)	44.5 (t)	46.7 (CH ₂) ^e	35.4 (t)	44.3 (t)				
15	49.2	50.0 (CH ₂) ^e	38.6 (CH ₂) ^e	43.6 (t)	46.6 (t)	41.0 (CH ₂) ^e	49.7 (t)	49.5	48.1 (t) ^a	82.6 (d)	82.3 (d)	209.7 (s)	46.5 (t)	45.3 (CH ₂) ^e	41.0 (d)	81.8 (d)				
16	155.7	155.4	160.3	156.5 (s)	156.2 (s)	154.3	153.8 (s)	153.3	157.6 (s)	161.3 (s)	159.7 (s)	150.4 (s)	155.7 (s)	157.9	157.8 (s)	163.3 (s)				
17	103.5	103.4 (CH ₂) ^e	106.8 (CH ₂) ^e	103.5 (t)	103.6 (t)	104.6 (CH ₂) ^e	104.6 (t)	106.4	102.9 (t)	107.7 (t)	104.3 (t)	113.8 (t)	103.6 (t)	102.9 (CH ₂) ^e	104.5 (t)	107.2 (t)				
18	29.3	29.2 (CH ₃) ^e	25.6 (CH ₃) ^e	29.3 (q)	28.6 (q)	28.5 (CH ₃) ^e	29.4 (q)	29.4	29.3 (q)	29.3 (q)	29.3 (q)	29.3 (q)	33.3 (q)	29.2 (CH ₃) ^e	29.2 (q)	29.3 (q)				
19	179.9	181.9	182.2	180.1 (s)	178.2 (s)	<i>d</i>	180.0 (s)	180.0	180.0 (s)	180.3 (s)	180.4 (s)	179.8 (s)	181.3 (s)	180.5	180.4 (s)	180.2 (s)				
20	16.0	18.6 (CH ₃) ^e	19.5 (CH ₃) ^e	16.3 (q)	15.7 (q)	15.2 (CH ₃) ^e	14.7 (q)	16.4	15.9 (q)	16.3 (q)	16.3 (q)	15.9 (q)	17.2 (q)	15.9 (CH ₃) ^e	16.1 (q)	16.2 (q)				

ⁱ Internal SiMe₄. ^e External SiMe₄. ^{a,b,c} Signals may be interchanged within each column. ^f Resonance not observed. ^g Assigned by d.e.p.t. ^h Assigned by off-resonance decoupling.

Table 3. Predicted ^{13}C chemical shifts for disubstituted *ent*-kaur-16-en-19-oic acid. δ (predicted) = (difference A) + (difference B) + δ (unsubstituted compound) (kaur-16-en-19-oic acid)

Carbon	(17)		(18)		(19)	
	Predicted	Observed	Predicted	Observed	Predicted	Observed
1	40.9	41.0	40.9	41.0	41.2	41.1
2	19.7	19.9	19.8	19.9	19.9	19.8
3	38.5	38.8	38.6	38.7	38.8	38.7
4	43.8	43.5	43.8	43.5	44.0	^a
5	49.5	48.7*	49.1	47.1*	57.2	57.2
6	30.5	30.7	30.3	30.6	22.2	22.1
7	76.5	76.3	74.3	78.0*	37.0	36.3*
8	46.3	46.3	50.8	48.3*	45.7	46.5*
9	46.5	47.4*	38.2	42.1	53.1	53.2
10	39.4	39.7	39.2	39.4	40.1	40.1
11	20.7	20.6	18.3	18.0	20.9	20.5
12	41.4	41.4	34.9	34.4	40.5	40.6
13	79.9	79.9	40.7	41.0	78.4	78.9
14	46.6	46.7	36.0	35.4*	43.9	44.3
15	45.5	45.3	79.7	82.7*	81.5	81.8
16	158.1	157.9	160.2	157.8*	163.2	163.3
17	103.0	102.9	104.4	104.5	107.1	107.2
18	28.6	29.2*	28.6	29.2*	29.3	29.3
19	178.3	180.5*	178.7	180.4*	180.4	180.2
20	15.6	15.9	15.9	16.1	16.2	16.2

^a Resonance not observed. * Difference between observed and predicted is >0.5 p.p.m.

capable of shielding C-9. Both the 6- and 15-ketones shift C-1 from its position in the spectrum of parent acid (1); the former deshielding and the latter shielding.

In an effort to examine the possibility of prediction of chemical shifts of polysubstituted *ent*-kaurenoic acids, the spectrum of each monosubstituted derivative was subtracted from that of the parent acid (1). The differences (A, B) in the chemical shift of each carbon atom resulting from the introduction of hydroxy groups at each position were found to be additive, and may be used to estimate the chemical shifts for each combination of hydroxylation positions. The value of such calculations is illustrated in Table 3, where the observed data for the three available disubstituted acids (17), (18), and (19) are compared with their predicted values, calculated as described above. For *ent*-13,15 β -dihydroxykaurenoic acid (19) only two carbon atoms show a difference from the predicted value of greater than 0.5 p.p.m. In the case of *ent*-7 α ,13-dihydroxykaurenoic acid (17), four carbon atoms show such deviation from their predicted values. The spectra of these compounds, therefore, show good agreement with the predicted spectra. For *ent*-7 α ,15 α -dihydroxykaurenoic acid (18), however, there are nine carbon atoms showing disagreements of greater than 0.5 p.p.m. The scale and number of these disagreements, which occur mainly in the B- and D-ring, are attributed to a change in conformation of these rings caused by the closeness of the *ent*-7 α - and *ent*-15 α -hydroxy groups, and the *ent*-9 α -hydrogen. The spatial compression of these groups would be relieved by the adoption of the twist-boat conformation for ring B [cf. earlier discussion concerning kaurenolide (20)].

Additionally, it should be possible to estimate the ^{13}C n.m.r. spectrum of *ent*-6 α ,7 α -dihydroxykaurenoic acid (16) from a knowledge of the spectra of *ent*-kaurenoic acid (1) and its *ent*-7 α -

and *ent*-6 α -hydroxylated derivatives (6) and (3), if the above reasoning is valid in this case. This would provide a further test of the method. Unfortunately the *ent*-6 α -hydroxy compound (3) is, as yet, unprepared and data are not, therefore, available. Therefore, although this empirical means of prediction may be of assistance in the identification of new polysubstituted kaurenoic acids, care is required where steric interaction of the functional groups may occur.

Experimental

Spectra were determined at room temperature using either JEOL FX-90Q or JEOL FX-200 Fourier transform spectrometers operating at 22.50 or 50.10 MHz respectively. Proton-noise-decoupled spectra were obtained and multiplicities were assigned with the aid of either off-resonance decoupling, or d.e.p.t.¹⁵ techniques. Accordingly, signals are designated with the following symbols: primary (q, CH₃), secondary (t, CH₂), tertiary (d, CH), or quaternary carbon (s).

Samples were examined in either deuteriochloroform or perdeuteriopyridine, at concentrations of 50–500 mM, using the solvent deuterium signal as internal heteronuclear lock. Spectra were recorded relative to internal or external (*via* the central *ortho*-carbon signal of perdeuteriopyridine, at δ_{C} 123.5 p.p.m.) tetramethylsilane. Chemical shifts are considered accurate to ± 0.1 p.p.m.

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