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NMR SIGNALS OF METHYL GROUPS OF TRITERPENES WITH OXYGEN FUNCTIONS AT POSITIONS 2, 3 and 23

H. T. CHEUNG* and D. G. WILLIAMSON

Departments of Chemistry, University of Malaya, Kuala Lampur, Malaysia,
University of Hong Kong, Hong Kong, and University of Aberdeen, Aberdeen, Scotland

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Abstract—NMR signals are assigned to each of the Me groups in a number of triterpenes of the ursane, oleanane, and lupane series with oxygen functions mainly at positions 2, 3 and 23. From these assignments the additive shielding effects of various substituents on the Me resonance frequencies have been deduced. The application of such data to structural problems has been illustrated.

IT IS known that for steroid[1] and triterpene[2–11] skeletons, modifications in substitution pattern are accompanied by systematic changes in the NMR chemical shifts of the angular Me groups. Such changes are, to a first approximation, additive. A complete assignment of Me resonances in a series of compounds is therefore of use in the elucidation of related structures.

We present here the results of an analysis of the Me resonances of triterpenes of the ursane, oleanane and lupane groups with oxygen functions mainly at positions 2, 3 and 23. Earlier work of this nature on the olean-12-ene triterpenes has been directed either to the parent hydrocarbon[9] or to compounds with oxygen functions chiefly at rings E and D.[10, 11] No substantial prior analysis of the urs-12-ene system has been attempted.†

In the early work on lupane triterpenes[2] no distinction between the signals for the Me groups 23, 24 and 25 was possible. This difficulty was later overcome, in the case of the olean-12-ene series, by examination of deuterated derivatives,[9, 11] Complete assignment of Me signals was also achieved, for oleanane[10] and other groups,[6–8] by detailed analysis from internal evidence. The latter method has been followed, and the results for over 50 triterpenes are presented in Table 1. In determining the assignment, use was made of the known[10] shielding effect on Me signals of olean-12-ene substituted at position 3 by β-OH, β-OAc, or =O (Table 2a). It was assumed that such a set of values for Me groups 23, 24, and 25 (on ring A) may be extrapolated for use in other A/B *trans* triterpenes with a similar ring A. This is justified since values similar to those in Table 2a can be derived from the data[7, 8] on 4,4-dimethylcholestane and lanostane compounds.

As was pointed out,[9] the spectral analysis of the ursane group is complicated by the second-order perturbation effect[1b] exhibited by the two secondary Me resonances (C-29 and 30) (see I). Where not obscured by other signals (e.g. in Nos. 8–10, Table 1),

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[*] To whom enquiries are to be directed at the University of Hong Kong.

[†] A note on the assignment of methyl signals of six urs-12-ene triterpenes came to our notice when this paper was completed (R. Savoir, R. Ottinger, B. Tursch and G. Chiurdoglu, *Bull. Soc. Chim. Belges* **76**, 371 (1967).

TABLE 1

Compound No.	Skeleton	Substituents			Other structural Features	Resonance frequencies* of methyl							Remarks and Ref.
		2α	3β	23		23	24	25	26	27	28	29/30	
1	Methyl	H	(=O)	H	—	65	63	63	48·5	65	—	48–57[e]	
2	urs-12-en-	H	OH	H	—	58	47	55	45·5	64·5	—	*a*	
3	28-oate	H	OAc	H	—	52	52	57	45	65	—	*a*	*b*
4	(I)	OAc	OH	H	—	63	52	64	45	65	—	*a*	*c*
5		OAc	OAc	H	—	54–55	54–55	64	45	64	—	*a*	*c*
6		OH	OH	OH	—	—	49	61	44	65	—	*a*	20
7		OAc	OAc	OAc	—	—	54	66·5	46	66	—	*a*	
8		OH	—OC(CH$_3$)$_2$O—		—	—	64	62	44	66	—	48–57[d]	20
9		OAc	—OC(CH$_3$)$_2$O—		—	—	65	67	44	66	—	48–57[d]	20
10		OAc	OAc	OAc	6β-OH	—	77·5	89·5	65	62·5	—	48–57[d]	*h*
11		H	OAc	H	19α-OH					73	—	75/	*e*
12		OAc	OAc	H	19α-OH	55	55	64	42	72	—	75/59[e]	*b*
13		OH	OH	H	19α-OH	62	50	58·5	41·5	72·5	—	75/*a*	*f*
14	19ξ-Urs-13(18)-en-	H	OAc	H	—	50–51	50–51	53	50–51	66	—	65(J, 7Hz)/82	*b*
15	20β,28-olide (V)	OAc	OAc	H	—	53	53	61	49	67	—	65(J, 7Hz)/82	*b*
16	Methyl 11-	H	OAc	H	—	50–52	50–52	67	58	77	—	*a*	*g*, CCl$_4$
17	oxo-urs-12-	OAc	OAc	OAc	—	—	55	77·5	55	77·5	—	48–58[e]	21
18	en-28-oate	OH	OH	OH	—	—	50	73	54	78	—	49–58[e]	21
19	(II)	OH	—OC(CH$_3$)$_2$O—		—	—	66	74·5	54	79·5	—	48–59[e]	21
20	Methyl olean-	H	(=O)	H	—	66	62·5–64	62·5–64	48	69·5	—	55, 56·5	*i*
21	12-en-28-	H	OH	H	—	60	47·5	55·7	44·5	69	—	55–57, 55–57	*i*
22	oate (IIIa)	H	OAc	H	—	52	52	55–57·5	44·5	68·5	—	55–57·5, 55–57·5	*i*
23		H	OAc	OAc	—	—	50·5	58	44·5	67	—	54, 56	
24		OAc	OH	H	—	62	52	63	43	67·5	—	54, 55·5	20
25		OAc	OAc	H	—	53–56	53–56	63	44	68	—	53–56, 53–56	20
26		OAc	OAc	OAc	—	—	53·5	65	44	66·5	—	53·5, 55	*l*
26a		(β-OAc)	OAc	(COOCH$_3$)	—	—	82·5	71	43	67	—	53–54, 53–54	*t*

27		(β-OAc)	OAc	OAc	—	—	62	73	45·5	67	—	54·5, 55·5	*r*
27a		(β-OAc)	OAc	OAc	16β-OAc	—	62·5	74–75	46	74–75	—	60, 56	*s*
27b		(β-OH)	OH	OH	—	—	64	75·5	44	66	—	54, 55	*r*
28		OH	OH	H	—	62	49	57	44	68	—	54–56, 54–56	20
29		H	OH	OH	—	—	51	56·5	43	66	—	53·5, 54·5	20
30		OH	OH	OH	—	—	49	60	43	68	—	55·5, 56	
31		H	—OCH(CH$_3$)O—		—	—	64	57	43	68	—	54, 55	20
32		OH	—OC(CH$_3$)$_2$O—		—	—	64	62	43	68	—	54, 55·5	*l*
33		OAc	—OC(CH$_3$)$_2$O—		—	—	64·5	67	43	68	—	54, 55·5	*l*
34		OAc	OAc	OAc	19β-OH	—	54	66	46	68	—	54, 56	*j*
35	Olean-12-en-28-oic acid (IIIb)	OAc	OAc	H	—	53–57	53–57	63	45	68	—	53–57, 53–57	20
36	18α-Oleanan-13β, 28-olide (VI)	OH	OH	OH	—	—	50	59·5	69–70	69–70	—	54, 50	20
37		OH	—OCH(CH$_3$)O—		—	—	65	60	69	69	—	53, 50	20
38		OAc	—OCH(CH$_3$)O—		—	—	64	68–69	68–69	68–69	—	53, 50	20
39	Olean-12-ene (IIIc)	H	OAc	H	16α,21β,22α,28-OAc	52	52	58	55	78·5	—	55/63	*k*
40		H	OAc	(CHO)	16α,21β,22α,28-OAc	—	65·5	61	54·5	78·5	—	54·5/63	*k*
41		H	OAc	H	16α,21β,22α,24, 28-OAc	59	—	61	54·5	78	—	54·5/63	*k*
42	11-Oxo-olean-12-ene (IIId)	H	OH	H	30-COOH	61	49·5	69	69	83	50	74/—	*g*
43		H	OAc	H	30-COOH	53	53	70	70	83	51	74·5/—	*g*
44		H	OAc	H	30-COOH, 18α-H	53·5	53·5	69	74	82	45	79/—	*g*
45	Methyl lupan-28-oate (IV)	H	(=O)	H	20,29-ene	63·5	60	57–58	55	57–58	—	—/100	*q*
46		H	OH	H	20,29-ene	57–58	45·5	49·5	55	57–58	—	—/102	*p*
47		H	OAc	H	20,29-ene	50–52	50–52	50–52	55	57	—	—/102	
48		OH	OH	H	20,29-ene	60·5	48	54	55	58	—	—/102	20
49		OAc	OAc	H	20,29-ene	52·5	52·5	55	57–58	57–58	—	—/101	20
50		H	(=O)	H	—	65	62	56–57	56–57	56–57	—	45, 51·5[m]	*n*
51		H	OH	H	—	57·5	45	49·5	54	56·5	—	44·5, 51[m]	*n*
52		OAc	(=O)	H	—	66–67	72·5	66–67	55·5	58	—	45, 51[m]	20

Compound No.	Skeleton	Substituents			Other Structural Features	Resonance frequencies[*] of methyl							Remarks and Ref.
		2α	3β	23		23	24	25	26	27	28	29/30	
53	Ditto	OAc	OH	H	—	62	50·5	54	56	56	—	45, 51[m]	20
54		OAc	OAc	H	—	52–54	52–54	52–54	55·5	58	—	45, 51[m]	20
55		OH	OH	H	—	60	48	53–55	53–55	57	—	45, 51[m]	20

[*] In Hz relative to TMS, for $CDCl_3$ solutions measured at 60 MHz.

[a] Multiplet partly buried under other peaks.

[b] Data recorded by Potier *et al.*[14]

[c] Data kindly provided by Dr. J. McLean;[13] measured at 40 MHz but now converted to 60 MHz.

[d] Two perturbed doublets, see Fig. 1 and text.

[e] Frequencies recorded by Bermejo *et al.*[17]

[f] Data kindly provided by Dr. P. Potier.[14]

[g] Data kindly provided by Dr. S. Sternhell.[23]

[h] Data kindly provided by Dr. H. Pinhas.[15]

[i] Frequencies recorded and assigned by Tursch *et al.*[10]

[j] Frequencies recorded by Schneider *et al.*[16]

[k] Frequencies recorded and assigned by Ito and Ogino.[19]

[l] Data kindly provided by Professor K. Nakanishi.[24]

[m] Two doublets, $J_{H-Me} = 6$ Hz; *cf.* Ref. 2a.

[n] Measured at 100 MHz but now converted to 60 MHz.

[p] Frequencies recorded and assigned by Aplin *et al.*[12]

[q] Frequencies found are substantially the same as that recorded by Lehn *et al.*[2]

[r] Data kindly provided by Dr. R. A. Eade.[22]

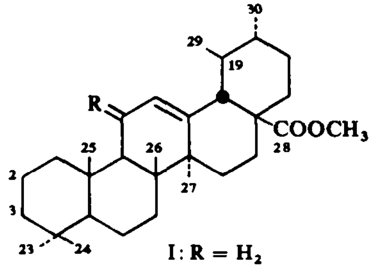
[s] Data recorded by Rondest and Polonsky.[17e]

[t] Data kindly provided by Professor R. J. Morris.[31]

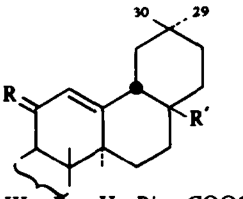
these Me resonances appear, at 60 MHz, as an AB_3-type signal (Fig. 1). In the case of the lupane triterpenes the well-defined splitting of the secondary Me resonances (see IV) has been discussed.[2a]

Fig. 1.

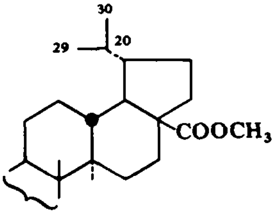
From the data in Table 1, deduction of the effect of a particular substituent on the Me resonances can be undertaken. The values (at 60 MHz) arrived at for both the urs-12-ene and the olean-12-ene skeleton are listed in Table 2b. Apart for minor differences, values derived from either skeleton are mutually applicable. In contrast, a different set of values is necessary for the structurally less similar lupane group, and it is listed separately in Table 2c. It is found that in two examples (Nos. 14, 15; 36–38) the effect of alterations to the ring skeletonon Me resonances is apparently also additive as is shown in Table 2d.



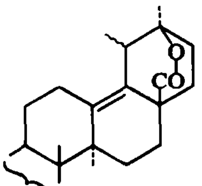
I: $R = H_2$
II: $R = O$



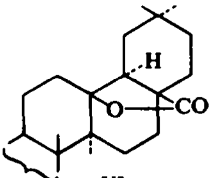
IIIa: $R = H_2$, $R' = COOCH_3$
IIIb: $R = H_2$, $R' = COOH$
IIIc: $R = H_2$, $R' = CH_3$
IIId: $R = O$, $R' = CH_3$



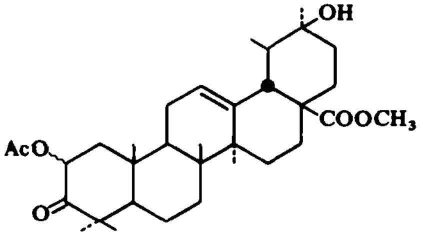
IV



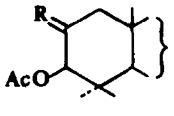
V



VI



VII



VIII: $R = O$
IX: $R = H_2$

TABLE 2a. EFFECT OF SUBSTITUENTS ON METHYL SIGNALS OF OLEAN-12-ENE (IIIc)[10] (AND URS-12-ENE)

Substituent	Increments in resonance frequencies* of methyl					
	23	24	25	26	27	29/30
3β-OH	+7	−2	+0·5	+1	0	0
3β-OAc	0	+3	+1	0	0	+0·5
3-Oxo	+13	+13	+8·5	+5·5	+0·5	0

* In Hz relative to TMS, for $CDCl_3$ solutions measured at 60 MHz.

TABLE 2b. EFFECT OF SUBSTITUENTS ON METHYL SIGNALS OF OLEAN-12-ENE (O) AND URS-12-ENE (U)

Substituent	Increments in resonance frequencies* of methyl						Skeleton from which data were computed
	23	24	25	26	27	29/30	
2α-OH	+2	+1·5	+1·5	−0·5	−0·5	−1[d]	(O), (U)
2α-OAc	+2·5	+2·5	+7·5	−0·5	−0·5	−1[d]	(O), (U)
2β-OH[b]	?	+13	+1·9	+1	0	+0·5	(O)
2β-OAc[b]	?	+10·5	+15·5	+1·5	0	0	(O)
23-OH[b]	—	+1	+1·5	−1·5	−1	−0·5[d]	(O), (U)
23-OAc[a]	—	−1·5	+2	+0·5	−1·5	−1	(O)
					+1	~0	(U)
23-CHO[b]	—	+13·5	+3	−0·5	0	0	(O)
23-COOCH$_3$[b]	—	+19	0	−2	−1·5	−2·5	(O)
24-OAc[b]	+7	—	+3	−0·5	−0·5	0	(O)
16β-OAc[b]	?	+0·5	+1·5	+0·5	+7·5	+5, +1	(O)
6β-OH[b]	?	+23·5	+23	+19	−3·5	~0	(U)
19β-OH[b]	?	+0·5	+1	+2	+1·5	+0·5	(O)
19α-OH	+0·5	+0·5	0	−3·5	+8	~22/?	(U)
30-COOH[c]	~+1	−1	0	0	+1	~20/—	(O)
11-oxo	~−1	+1·5	+12	+10	+13	~0	(U)
3β,23-isopropylidenedioxy	—	+12·5	+5	−0·5	+0·5	0[d]	(O) (U)
3β,23-ethylidenedioxy	—	+13	+2	−0·5	−0·5	−1	(O)

* In Hz relative to TMS, for $CDCl_3$ solutions measured at 60 MHz.

[a] Increments are similar to those one may calculate from the data recorded for the poly-acetates of camelliagenins A and C[18].

[b] Based on limited data, and confirmation is desirable.

[c] For calculation, effect of 28-COOCH$_3$ as given by Tursch *et al.*[10] employed.

[d] Applies only to skeleton (O).

Values of Me signals of the parent systems methyl olean-12-en-28-oate (IIIa) and methyl lupan-28-oate (IV) are available from the work of Tursch *et al.*[10] and of Lehn and Ourisson,[2a] and are listed in Table 3. Table 3 also shows similar data for methyl urs-12-en-28-oate (I), deduced from the present work. Calculated resonance frequencies based on Tables 2 and 3 agree with experimental values (Table 1) to within 2 Hz, attesting to the basic premise of additivity.

Marked deviation from additivity, however, is shown by the 2α-acetoxy-3-ketone (No. 52) of methyl lupan-28-oate, the experimental frequencies for Me groups 24 and 25 being respectively 10 and 6 Hz higher than calculated. Such anomaly in 2α-acetoxy-4,4-dimethylcholestan-3-one has been discussed by Hemmert *et al.*[8] in terms of the preferred orientation of the acetoxy carbonyl. A lesser anomaly (∼3Hz for C-23, 24 and 25) shown by the corresponding 2α-acetoxy-3β-ol (No. 53) could be similarly caused. Departure from additivity is expected to occur also in a molecule such as methyl bredemolate (methyl 2β, 3α-dihydroxy-olean-12-en-28-oate)* in which the presence of two axial OH groups is believed[25] to cause ring A to be distorted from the chair conformation.

It is pertinent to make some observations on the values presented in Tables 2b and 2c on the contribution of substituents to Me resonances. A 2α substituent is symmetrically placed with respect to Me 24 and 25 and is thus expected[1a, 26] to have similar effects on these Me groups. For urs-12-ene and olean-12-ene, values found for 2α-OH (+1·5, +1·5 Hz) are in agreement with the above deduction. In the case of 2α-OAc, however, the effect on Me 25 (+7·5 Hz) is significantly larger than that on Me 24 (+2·5 Hz). This is presumably because the acetoxy group adopts a conformation in which the deshielding cone of the carbonyl is directed towards Me 25. The above situation, however, apparently does not arise where the parent system is lupane (Table 2c).

TABLE 2c. EFFECT OF SUBSTITUENTS ON METHYL SIGNALS OF LUPANE

Substituent	Increments in resonance frequencies* of methyl					
	23	24	25	26	27	29/30
3β-OH	+7	−3	−1·5	−1·5	−0·5	0
3β-OAc	+1	+3	−1	−0·5	−0·5	0
3-oxo	+14	+13	+6	−0·5	0	0
2α-OH	+2·5	+2·5	+4·5	0	+0·5	0
2α-OAc	+1·5	+1·5	+3·5	+1	+0·5	0
(20-ene)	−0·5	−0·5	+0·5	0	0	−/∼+53

* In Hz relative to TMS, for $CDCl_3$ solutions measured at 60 MHz.

The 6β-OH group is in a 1:3 di-axial relationship with Me 24, 25, and 26 and is expected to deshield[27] each strongly. This is borne out in practice, the effect on these Me groups being of the order of 20 Hz.

Similarly, a 19α-OH causes a pronounced deshielding (8 Hz) of the spatially neighbouring Me 27, and the significance has been discussed by Potier[14] and González[17] and their respective coworkers.

In the following example, the utility of Me shifts data in structural determination

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* NMR spectrum kindly provided by Professor R. Tschesche.
Assignments: C-23, 24, 25   26   27   29/30
(54, 60, 65)   43   67   54, 54 Hz

TABLE 2d. EFFECT OF SKELETAL CHANGES

Skeletal change	Increments in resonance frequencies* of methyl					
	23	24	25	26	27	29/30
Methyl olean-12-en-28 oate → 18α-oleanan-13β-,28-olide (VI)	?	−0·5	+2	+26·5	0	−1, −3
Methyl urs-12-en-28-oate → 19ζ-urs-13(18)-en-20β,28-olide (V)	−1·5	−1·5	−3·5	+4·5	+2	?

* In Hz relative to TMS, for $CDCl_3$ solutions measured at 60 MHz.

TABLE 3. "PARENT" SYSTEMS

Compound	Resonance frequencies* of methyl						Ref.
	23	24	25	26	27	29/30	
Methyl urs-12-en-28-oate (I)	52	49·5	55·5	45	65	48–57 mult.	This work
Methyl olean-12-en-28-oate (IIIa)	52·5	50	55·5	43·5	69	55·5, 56	10
Methyl lupan-28-oate (IV)	50·5	48·5	51·5	56	57·5	45, 51	2a

* In Hz relative to TMS, for $CDCl_3$ solutions measured at 60 MHz.

TABLE 4.

	Resonance frequencies* of methyl					
	23	24	25	26	27	29/30
Expt. value† for 3β-acetate IX	52	52	57	42	73·5	—/75·5
Expected[a] for 2α-acetoxy-3-one VII	67·5	>65	>71·5	47	73·5	—/75
Calc.[b] for 2β-acetoxy-3-one VII	67	73	80	49	74	—/75
Calc.[c] for 3β-acetoxy-2-one VIII	66	50·5	56	42	73·5	—/75
Found†	67	52	55	42	73·5	—/79

[a] See text, above.

[b] Effect of 2β-OAc on methyl 23 as recorded by Hemmert *et al.*[8] = +2 Hz.

[c] Effect of (3β-OAc + 2-oxo) on methyl groups 23, 24 and 25 adopted from data of Hemmert *et al.*[8]: +14, +1, −0·5 Hz; that on 26 and 27 assumed to be negligible.

* In Hz relative to TMS, for $CDCl_3$ solutions measured at 60 MHz.

† We are grateful to Dr. J. McLean for kindly putting at our disposal his unpublished data (measured at 40 MHz, but now converted to 60 MHz for computation).

has been illustrated. A triterpene which was given a 2ξ-acetoxy-3-one structure VII[28] shows Me resonances† which do not accord with such formulation (Table 4). However, good agreement with values calculated for the corresponding 3β-acetoxy-2-one structure VIII is noted by us (Table 4). In confirmation, the low field region of the NMR spectrum is found to show a sharp one-proton singlet at τ 5·03,† a signal which is incompatible with structure VII but which may be assigned to the unflanked C-3 proton in structure VIII. A similar signal near τ 5 had been recorded for the 3α-proton in 3β-acetoxy-2-ones of the 4,4-dimethylcholestane, 8-lanostene,[30] and 8-euphene series.[29]

EXPERIMENTAL

Unless stated otherwise, NMR spectra were determined at 60 MHz on 5–15% (w/v) solutions in $CDCl_3$ on the Varian A-60 or Hitachi H-6013 spectrometer. Resonance frequencies quoted referred to TMS as internal standard. Unless referred to otherwise, and excepting compounds 1 and 2 (Table 1), triterpenes samples used were prepared at the University of Malaya.[20,21]

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† We are grateful to Dr. J. McLean for kindly putting at our disposal his unpublished spectral data (measured at 40 MHz, but now converted to 60 MHz for computation).

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