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TRITERPENES VIII(°). NMR SPECTRA OF TRITERPENES. EFFECT OF SUBSTITUTION ON THE CHEMICAL SHIFTS OF METHYL GROUPS IN THE Δ^{12}-OLEANENE SERIES.

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In a previous communication (1) the methyl region of the NMR spectrum of some Δ^{12}-oleanene derivatives has been completely or partially assigned. However no discrimination between the absorptions of methyls 23, 24 and 25 was achieved at that time.

Examination of the NMR spectra of a further series of Δ^{12}-oleanene derivatives and critical comparison with literature data on ring A of 4,4-dimethylsteroids (2,3) have cleared up that difficulty and led to the complete assignment of the methyl peaks of Δ^{12}-oleanene (°°) :

Methyls :	23	24	25	26	27	28	29	30
Frequencies in cps (°°°) :	53	50.5	56.5	59	69	50.5	53	53

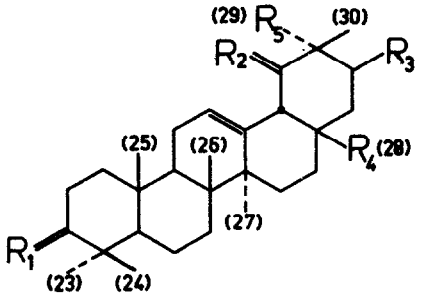
The frequencies found for methyls 27, 28, 29 and 30 are in agreement with the conclusions of Karliner and Djerassi (4) who have selectively deuteriated methyls 28 and 30.

The following compounds have been used in the present work :

(°) Part VII. D.Daloze, B.Tursch, G.Chiurdoglu, *Bull.Soc.Chim.Belg.* in press.

(°°) A full paper describing the method will shortly appear elsewhere.

(°°°) All data refer to 60 Mc spectra, $CDCl_3$, TMS=0.



	R_1	R_2	R_3	R_4	R_5
I	H_2	H_2	H	Me	Me
II	βOH,αH	H_2	H	Me	Me
III	βOAc,αH	H_2	H	Me	Me
IV	βOBz,αH	H_2	H	Me	Me
V	O	H_2	H	Me	Me
VI	H_2	H_2	H	COOH	Me
VII	H_2	H_2	H	COOMe	Me
VIII	H_2	H_2	H	$CONH_2$	Me
IX	H_2	H_2	H	CN	Me
X	H_2	H_2	H	CH_2I	Me
XI	H_2	H_2	H	CH_2OTos	Me
XII	βOH,αH	H_2	H	COOMe	Me
XIII	βOAc,αH	H_2	H	COOMe	Me
XIV	O	H_2	H	COOMe	Me
XV		H_2	H	COOMe	Me
XVI	βOAc,αH	H_2	H	COOH	Me
XVII	O	H_2	H	COOH	Me
XVIII	βOAc,αH	H_2	H	CHO	Me
XIX		H_2	H	CH_2OH	Me
XX	O	H_2	H	CH_2OH	Me
XXI	O	H_2	H	CH_2OTOs	Me
XXII	αOH,βH	H_2	H	Me	COOH
XXIII	βOH,αH	αOH,βH	H	COOMe	Me
XXIV	βOAc,αH	αOH,βH	H	COOMe	Me
XXV	βOAc,αH	O	H	COOMe	Me
XXVI	βOH,αH	H_2	OH	COOMe	Me
XXVII	βOAc,αH	H_2	OH	COOMe	Me
XXVIII	βOAc,αH	H_2	OAc	COOMe	Me
XXIX	O	H_2	28:21β-olide		Me
XXX	βOAc,αH	H_2	28:21β-olide		Me
XXXI	βOH,αH	H_2	H	COOMe	CH_2OH
XXXII	βOH,αH	H_2	H	COOMe	COOH
XXXIII	βOAc,αH	H_2	H	COOMe	COOMe
XXXIV	O	H_2	H	COOMe	COOH
XXXV	βOH,αH	H_2	H	CH_2OH	Me
XXXVI	βOH,αH	H_2	H	COOMe	COOMe
XXXVII	βOAc,αH	H_2	H	COOMe	CH_2OAc
XXXVIII	O	H_2	H	Me	COOMe

The observed methyl frequencies and their assignment are listed in Table I.

TABLE I.

Observed Methyl Frequencies.

	Me 23	Me 24	Me 25	Me 26	27	28	Me 29 and/or 30	
I	53	50.5	56.5	59	69	50.5	53	53
II	59.5	48	57	60.5	69	51	53	53
III	53	53	57.5-59	57.5-59	68.5	50.5	53	53
IV	57.5	60.5-62	60.5-62	60	69.5	51	53	53
V	66	62	64	65	69	51	53	53
VI	52	49	54.5-56.5	45.5	69		54.5-56.5	54.5-56.5
VII	52	49	54.5-56	44	68.5		54.5-56.5	54.5-56.5
VIII	52.5	50.5	54.5-56.5	50.5	71		54.5-56.5	54.5-56.5
IX	52.5	50	55	62.5	69		57	57
X	52-54	49.5	55.5	55.5	70.5		52-54	52-54
XI	51.5-53.5	49	51.5-53.5	33.5	66.5		51.5-53.5	51.5-53.5
XII	60	47.5	55-57	44.5	69		55-57	55-57
XIII	52	52	55-57.5	44.5	68.5		55-57.5	55-57.5
XIV	66	62.5-64	62.5-64	48	69.5		55	56.5
XV	51.5	55-57	55-57	44	69		55-57	55-57
XVI	52	52	55-57	45.5	69		55-57	55-57
XVII	65.5	62-63.5	62-63.5	49	69		55-56.5	55-56.5
XVIII	52	52	55-57.5	45	69		55-57.5	55-57.5
XIX	52	57	57	59	71		53	53
XX	65.5	60.5	63.5	64	71		53	53
XXI	65	62.5	63	39.5	67		50.5-52.5	50.5-52.5
XXII	58	51.5	58	58	69.5	51.5		74
XXIII	58-59	47	54.5	44	75.5		58-59	58-59
XXIV	52	52	56	45	75.5		58.5	58.5
XXV	52	52	57.5	45.5	60		65.5	71.5
XXVI	59	47	55	43.5	68		55	59
XXVII	52	52	56	44	68		56	59
XXVIII	51.5-53	51.5-53	56	44	68		51.5-53	59
XXIX	66	63	63	49	66		61	61
XXX	52	52	56	45	66		61	61
XXXI	60	47	56	45	69			58
XXXII	59	47	55	44	68.5			78
XXXIII	52	52	57	44	68.5			76
XXXIV	66	63	63	48	70			78
XXXV	59	47	56	56	69.5		52.5	52.5
XXXVI	60	47	55	44	69			76
XXXVII	52	52	57	44	68			60
XXXVIII	66	62	64	64	69	52		72

From these data one can deduce the effect of a given substituent on the methyl resonance frequencies in the Δ^{12}-oleanene group, thus extend to that series the work of Zürcher (5) in the steroid field. The suggested values are listed in Table II.

TABLE II

Effect of Substituents on the Chemical Shift of Methyl Groups

Substituent	Effect on Methyl							
	23	24	25	26	27	28	29	30
3β-OH	+7	-2	+0.5	+1	0	+0.5	0	0
3β-OAc	0	+3	+1	0	0	0	+0.5	+0.5
3β-OBz	+4.5	+10.5	+4.5	+1	+0,5	+0.5	0	0
3-Oxo	+13	+13	+8,5	+5,5	+0.5	+0.5	0	0
3-Ethylene ketal	?	?	?	0	+0.5	?	+0,5	+0.5
19α-OH	-0.5	0	-0.5	0	+6.5	?	+2.5	+2.5
19-Oxo	0	0	+1.5	+1	-8.5	?	+9.5[a]	+15.5[a]
21β-OH	-0.5	0	-0.5	-0.5	-0.5	?	-0.5[a]	+3[a]
21β-OAc	0	0	0	-0.5	-0.5	?	-4[a]	+3[a]
28-COOMe	-0.5	-0.5	-1	-15.5	0	-	+2.5	+3
28-COOH	-1	-0.5	-1.5	-14	0	-	+2.5	+2.5
28-CHO	-1	-1	-2	-13	+0.5	-	+3	+3
28:21β-olide	-0.5	0	-1.5	-14.5	-2.5	-	+8	+8
28-OH	-0.5	-1.5	-0.5	-1	+2	-	0	0
28-I	0	-1	-1	-3.5	+1.5	-	0	0
28-OTos	-0.5	-0.5	-2.5	-25.5	-2	-	-1	-1
28-CN	-0.5	-0.5	-1.5	+3.5	0	-	+4	+4
28-$CONH_2$	-0.5	0	-1	-8.5	+2	-	+2.5	+2.5
29-COOH	-0.5	0	-0.5	0	0	?	-	+22
29-OH	0	-0.5	0	+0.5	0	?	-	+2
29-COOMe	0	0	+1	-0.5	0	?	-	+20
29-OAc	0	0	+1	-0.5	-0.5	?	-	+4

[a] Values for C-29 and C-30 might have to be inverted.

Example : compound XXXI

	Me 23	Me 24	Me 25	Me 26	Me 27	Me 30
Oleanene	53	50.5	56.5	59	69	53
3β-OH	+7	-2	+0.5	+1	0	0
28-COOMe	-0.5	-0.5	-1	-15.5	0	+3
29-CH_2OH	0	-0.5	0	+0.5	0	+2
Calculated	59.5	47.5	56	45	69	58
Measured	60	47	56	45	69	58
Error	0.5	0.5	0	0	0	0

For all the compounds examined here, the average error is less than 0.5 cps, the maximum error being 3 cps.

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