

¹³C NMR SPECTRA OF OLEAN-18-ENE DERIVATIVES

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Key Word Index—Triterpenes; germanicol; olean-18-ene derivatives; ¹³C NMR analysis.

Abstract—The ¹³C NMR signals of sixteen derivatives of olean-18-ene-triterpenes have been assigned.

For the last few years considerable interest has been focused on the ¹³C NMR spectral analysis of triterpenes, especially of the olean-12-ene [1–5] and urs-12-ene [6, 7] series. Other work in the field has dealt with lanosterol [5, 8], cycloartenol [9], euphol [5], limonoids [10] and dammarane derivatives [11]. Recently the ¹³C NMR spectra of triterpenes related to lupane and hopane have been published [12].

From *Salvia broussonetti* germanicol (olean-18-ene-3 β -ol) and its 1 β -hydroxy and 11 α -hydroxy derivatives (anagadiol [13] and nivadiol [14]) have been isolated. Later the synthesis of anagadiol was reported [15]. The availability of these natural products and their synthetic derivatives prompted us to undertake a ¹³C NMR study of the olean-18-ene series as a continuation of our studies on the NMR spectra of natural products. Until now, only the spectra of two morolic acid derivatives [16] and partial data on germanicol [17] have been published. The present work deals with the complete experimental assignment of the carbon frequencies of sixteen olean-18-ene derivatives.

The signals were assigned by means of SFORD and NORD experiments, using shift reagent techniques, by applying known chemical shift rules and by comparison with the spectra of related compounds.

Inspection of Table 1 shows that for germanicol (1) the experimental values of C-1 to C-14 agree reasonably well with those calculated by Beierbeck and Saunders [17] and also as expected with those experimentally obtained for lupeol [12].

From the data presented in Tables 1 and 2, the substitution effects of an equatorial hydroxyl group at C-1 and C-11, an equatorial acetoxy or axial hydroxyl group at C-11 and a keto function at C-11 or C-16 can be calculated and these values may also be useful for further studies in this field.

EXPERIMENTAL

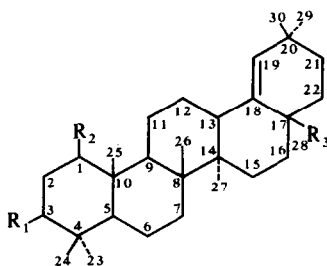
All the ¹³C NMR spectra (except for compound 10) were determined on a Varian CFT-20 operating at 20.00 MHz and running with a width of 5000 or 4000 Hz with 8 K points and 10000–50000 transients depending on the terpene concn. The spectrum of 10 was recorded on a Jeol PFT 100 operating at 25.15 MHz. The spectral width was 6250 Hz; 8 K data points were used for 4300 accumulations. The spectra were measured in CDCl₃ solns and TMS was used as an internal standard in every case.

Compounds investigated. 3 β -Hydroxy-olean-18-ene, germanicol (1); 3 β -acetoxy-olean-18-ene, germanicol acetate (2); 1 β ,3 β -dihydroxy-olean-18-ene, anagadiol (3); 1 β -hydroxy-3 β -acetoxy-olean-18-ene, anagadiol 3 β -monoacetate (4); 3 β -acetoxy-olean-18-en-28-oic, morolic acid acetate (5); 3 β ,28-diacetoxy-olean-18-ene, moradiol diacetate (6); 3 β -acetoxy-28-hydroxy-olean-18-ene, moradiol 3 β -monoacetate (7); 3-oxo-olean-18-ene, germanicone (8); 3,11-dioxo-olean-18-ene (9); 3,16-dioxoolean-18-ene (10); 3 β ,11 α -dihydroxy-olean-18-ene, nivadiol (11); 3 β ,11 α -diacetoxy-olean-18-ene, nivadiol diacetate (12); 3 β ,11 β -dihydroxy-olean-18-ene (13); 3 β ,11 β -diacetoxy-olean-18-ene (14); 3-oxo-olean-1,18-diene (15); 1 α ,2 α -epoxy-3-oxo-olean-18-ene (16).

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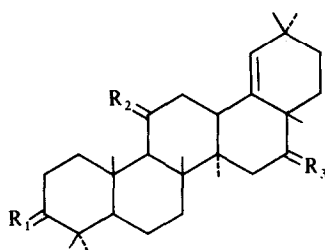
1. Dodrell, D. M., Khong, P. W. and Lewis, K. G. (1974) *Tetrahedron Letters* 2381.



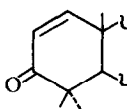
	R ₁	R ₂	R ₃
1	OH	H	Me
2	OAc	H	Me
3	OH	OH	Me
4	OAc	OH	Me
5	OAc	H	CO ₂ H
6	OAc	H	CH ₂ OAc
7	OAc	H	CH ₂ OH

Table 1. ^{13}C NMR chemical shifts of compounds 1–8

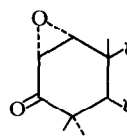
	1	2	3	4	5	6	7	8
C-1	38.5	38.5	75.7	77.5	38.7	38.7	38.7	39.9
C-2	27.4	23.8	39.0	34.0	23.7	23.7	23.7	34.0
C-3	79.0	81.0	79.5	78.9	81.0	80.9	81.0	217.8
C-4	39.0	37.9	38.4	37.8	37.9	37.8	37.8	47.2
C-5	55.7	55.7	53.4	53.3	55.7	55.6	55.6	55.0
C-6	18.3	18.2	18.0	17.9	18.2	18.2	18.2	19.7
C-7	34.7	34.6	34.6	34.5	34.5	34.6	34.6	34.0
C-8	40.8	40.9	41.4	41.4	40.8	40.9	40.9	40.7
C-9	51.3	51.2	52.4	52.3	51.2	51.2	51.1	50.6
C-10	37.3	37.3	43.8	43.4	37.2	37.2	37.2	37.0
C-11	21.2	21.2	23.9	23.8	21.0	21.1	21.0	21.7
C-12	26.2	26.2	26.2	26.2	26.0	26.3	26.2	26.3
C-13	39.0	38.7	38.1	38.1	41.3	38.9	38.7	38.6
C-14	43.4	43.4	43.5	43.4	42.7	43.1	43.2	43.4
C-15	27.6	27.6	27.5	27.6	29.4	27.4	27.3	27.6
C-16	37.7	37.7	37.8	37.7	33.5	31.4	31.6*	37.7
C-17	34.4	34.4	34.4	34.3	48.0	37.9	39.6	34.4
C-18	142.8	142.7	142.7	142.6	136.7	138.2	138.7	142.6
C-19	129.8	129.8	129.7	129.7	133.1	133.7	134.4	130.0
C-20	32.3	32.4	32.4	32.3	32.1	32.2	32.3	32.4
C-21	33.4	33.4	33.5	33.4	33.5	32.9	33.3	33.4
C-22	37.4	37.5	37.5	37.4	33.5	31.4	31.4*	37.4
C-23	28.0	28.0	28.0	27.8	28.0	27.9	27.9	26.9
C-24	15.4	16.5	15.1	16.5	16.5	16.5	16.5	21.0
C-25	16.1	16.1	12.5	12.7	16.0	16.2	16.2	16.0
C-26	16.7	16.8	16.5	16.2	16.7	16.7	16.7	16.0
C-27	14.6	14.5	14.5	14.5	14.9	14.8	14.7	14.5
C-28	25.3	25.3	25.4	25.3	182.8	65.8	65.4	25.3
C-29	31.3	31.3	31.3	31.3	30.3	30.9	30.6	31.3
C-30	29.2	29.2	29.3	29.3	29.1	29.4	29.8	29.2



	R_1	R_2	R_3
8	O	H_2	H_2
9	O	O	H_2
10	O	H_2	O
11	OH	H	H_2
12	OAc	H	H_2
13	OH	OH	H_2
14	OAc	OAc	H_2



15



16

Table 2. ¹³C NMR chemical shifts of compounds 9–16

	9	10	11	12	13	14	15	16
C-1	38.9	39.7	41.4	40.5	39.0	38.7	159.8	56.9
C-2	34.1	33.9	27.7	23.9	27.3	23.6	125.2	63.9
C-3	216.6	217.8	78.5	80.3	78.9	80.8	205.0	212.5
C-4	47.5	47.1	39.1	38.3	38.9	37.8	44.6	44.7
C-5	55.3	54.6	55.9	55.6	56.4	56.5	53.8	45.8*
C-6	19.3	19.6	18.0	17.9	18.5	18.4	19.9	18.9
C-7	33.0*	33.9	35.6	35.3	36.3	36.3	34.1	33.8†
C-8	45.8	40.3	42.9	43.0	41.2	41.2	39.5	41.1
C-9	63.0	49.8	56.5	53.4	53.4	53.3	45.2	44.1*
C-10	36.2	36.9	39.5	38.6	38.4	37.8	41.6	38.5
C-11	211.8	21.4	71.1	73.2	67.4	67.4	21.4	22.1
C-12	44.4	26.1	38.6	33.2	36.3	36.3	26.1	26.6
C-13	40.3	38.5	37.3	37.0	32.8	32.8	38.6	38.5
C-14	43.3	49.7	43.0	43.0	43.3	43.3	43.5	43.4
C-15	27.3	45.3	27.5	27.4	27.6	27.5	27.5	27.6
C-16	37.2	216.1	37.6	37.5	37.6	37.6	37.6	37.6
C-17	34.6	45.0	34.3	34.3	34.5	34.5	34.3	34.4
C-18	140.4	139.8	141.6	141.1	142.5	142.4	142.3	142.3
C-19	130.4	132.9	129.9	130.0	130.0	130.0	129.9	130.0
C-20	32.3	32.2	32.4	32.4	32.4	32.4	32.3	32.3
C-21	33.1*	32.6	33.4	33.3	33.3	33.3	33.3	33.7†
C-22	37.2	28.0	37.3	37.3	37.4	37.4	37.4	37.4
C-23	26.2	25.8	28.2	28.2	28.2	28.1	27.8	27.8
C-24	21.5	20.9	15.6	16.6	15.5	16.5	21.4	20.8
C-25	15.9	16.3*	17.4	17.3	20.0*	20.0*	19.0	15.8
C-26	17.4	16.5*	16.9	17.0	18.1*	18.1*	16.7	16.6
C-27	14.2	14.9	14.3	14.2	14.7	14.6	14.7	14.4
C-28	25.1	27.0	25.3	25.2	25.2	25.1	25.3	25.3
C-29	31.1	31.2	31.3	31.1	31.3	31.3	31.3	31.3
C-30	29.1	28.7	29.2	29.1	29.2	29.2	29.2	29.3

Data on OAc signals are not described.

*,†Assignments may be reversed in each vertical column but those given here are considered most likely.

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