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CARBON-13 NMR SPECTRA OF OLEAN-12-ENES.
FULL SIGNAL ASSIGNMENTS INCLUDING QUATERNARY CARBON SIGNALS ASSIGNED BY USE OF INDIRECT $^{13}C,^{1}H$ SPIN COUPLINGS

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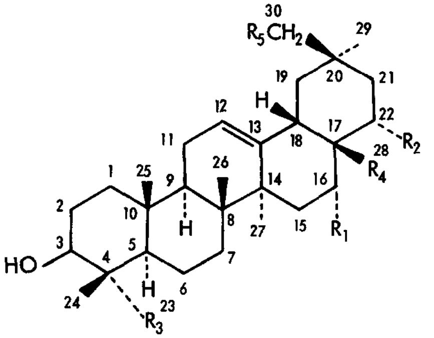
A number of triterpenes having an olean-12-ene skeleton have been isolated from plants.[1] Full assignments of ^{13}C NMR signals of this type of compounds are quite desirable from the view-point of their biosynthetic studies as well as structural elucidation. Quite recently, Doddrell, et al.[2] have reported ^{13}C NMR spectra of several olean-12-enes and urs-12-enes in pyridine. However, their spectral assignments are limited to signals due to olefinic C-12 and C-13, and carbons bearing an OH group. Having been prompted by this paper, we report here our full signal assignments for ^{1}H noise-decoupled natural-abundance ^{13}C FT NMR spectra of methyl esters of oleanolic acid (1), hederagenin (2), queretaroic acid (3), gypsogenin (4), and quillaic acid (5), 22α- (6) and 23-hydroxyerythrodiols (7), and their peracetates in $CDCl_3$.



	R_1	R_2	R_3	R_4	R_5
(1)	H	H	Me	CO_2Me	H
(2)	H	H	CH_2OH	CO_2Me	H
(3)	H	H	Me	CO_2Me	OH
(4)	H	H	CHO	CO_2Me	H
(5)	OH	H	CHO	CO_2Me	H
(6)	H	OH	Me	CH_2OH	H
(7)	H	H	CH_2OH	CH_2OH	H

The signal assignments were generally carried out by means of known chemical-shift rules[3] such as hydroxyl substitution shifts, acetylation shifts, and steric γ and δ[4] effects, single-frequency off-resonance decoupling (SFORD)[3] and/or noise off-resonance decoupling (NORD)[5] techniques, and chemical-shift (δ_C) comparisons from compound to compound. The Table lists δ_C values determined.

TABLE. Carbon-13 Chemical Shifts (δ_C) of Olean-12-enes (1-7) and Their Peracetates (in Parentheses) in $CDCl_3$[a]

Carbon	(1)	(2)	(3)	(4)	(5)	(6)[c]	(7)[c]
C-1	38.5(38.1)	38.1(37.7)	38.7(38.1)	38.0(37.7)	38.1(37.8)	39.0(38.3)	38.3(37.9)
C-2	27.1(23.6)	26.4(23.0)	27.0(23.4)	26.0(22.5)	26.0(22.5)	27.0(23.6)	26.0(23.0)
C-3	78.7(80.7)	76.4(74.3)	78.9(80.7)	71.8(73.2)	71.7(73.2)	78.8(80.7)	75.7(74.6)
C-4	38.7(37.5)	41.7(40.6)	38.7(37.7)	55.2(54.2)	55.2(54.2)	39.0(37.7)	41.7(40.6)
C-5	55.2(55.2)	49.7(47.7)	55.3(55.2)	48.0(47.7)	48.1(47.9)	55.6(55.2)	49.3(47.9)[b]
C-6	18.3(18.2)	18.5(18.1)	18.5(18.2)	20.7(20.3)	20.7(20.3)	18.6(18.2)	18.3(18.0)
C-7	32.6(32.6)	32.4(32.3)	32.8(32.6)	32.3(32.2)	32.3(32.3)	32.8(32.5)	32.3(32.2)
C-8	39.3(39.3)	39.3(39.3)	39.3(39.3)	39.6(39.5)	39.7(39.7)	40.2(40.0)	39.7(39.8)
C-9	47.6(47.5)	47.5(47.7)	47.7(47.5)	47.5(47.5)	46.7(46.6)	47.9(47.5)	47.4(47.7)[b]
C-10	37.0(36.9)	36.9(36.8)	37.2(36.9)	36.0(35.7)	35.9(35.8)	37.1(36.8)	36.8(36.7)
C-11	23.1(23.0)	23.1(23.0)	23.4(23.4)	23.0(22.8)	23.2(23.2)	23.8(23.6)	23.6(23.6)
C-12	122.1(122.1)	122.2(122.0)	122.8(122.7)	121.9(121.7)	122.2(123.0)	123.0(123.8)	122.1(122.6)
C-13	143.4(143.6)	143.6(143.6)	143.2(142.9)	143.6(143.6)	142.8(141.9)	143.2(141.9)	144.2(143.6)
C-14	41.6(41.6)	41.7(41.6)	41.7(41.4)	41.7(41.5)	41.4(41.0)	41.5(41.7)	41.7(41.6)
C-15	27.7(27.7)	27.7(27.7)	27.7(27.5)	27.6(27.6)	35.4(32.3)	25.3(25.0)	25.6(25.6)
C-16	23.4(23.6)	23.4(23.4)	23.4(23.4)	23.3(23.2)	74.7(76.0)	14.7(16.7)	21.9(22.2)
C-17	46.6(46.6)	46.7(46.6)	46.8(46.4)	46.6(46.5)	48.7(47.5)	43.0(40.1)	36.8(35.8)
C-18	41.3(41.3)	41.3(41.3)	40.3(40.7)	41.3(41.2)	40.5(40.3)	42.4(41.9)	42.5(42.6)
C-19	45.8(45.8)	45.9(45.8)	40.3(41.4)	45.8(45.7)	46.4(46.1)	46.0(44.1)	46.6(46.2)
C-20	30.6(30.6)	30.7(30.6)	35.2(33.7)	30.7(30.5)	30.3(30.3)	31.5(31.5)	30.9(30.9)
C-21	33.8(33.8)	33.9(33.8)	32.8[b](29.3)[b]	33.8(33.7)	35.4(35.0)	42.4(38.9)	34.2(34.0)
C-22	32.3(32.3)	32.4(32.3)	32.1[b](31.7)[b]	32.1(31.9)	30.3(30.9)	75.8(71.7)	30.9(31.4)
C-23	28.1(28.0)	71.3(65.3)	28.1(28.0)	207.0(204.0)	207.0(204.0)	28.2(28.0)	70.3(65.4)
C-24	15.6[b](16.8)	11.6(13.1)	15.7(16.7)	8.9(9.5)	9.0(9.5)	15.6(16.7)	11.6(13.1)
C-25	15.3[b](15.3)	15.7(15.8)	15.4(15.4)	15.5(15.5)	15.7(15.6)	15.6(15.5)	15.9(16.0)
C-26	16.8(16.8)	16.9(16.8)	16.9(16.7)	16.8(16.7)	16.9(16.8)	16.7(16.7)	16.7(16.7)
C-27	26.0(25.8)	26.0(25.8)	26.0(25.9)	26.0(25.8)	27.0(26.4)	26.4(26.2)	26.0(25.8)
C-28	177.9(177.8)	178.2(177.8)	178.5(177.4)	177.9(177.7)	177.2(175.6)	70.1(66.0)	69.1(70.7)
C-29	33.1(33.1)	33.1(33.1)	28.9(27.8)	33.1(33.0)	32.7(33.1)	33.4(33.0)	33.2(33.1)
C-30	23.6(23.6)	23.6(23.6)	65.8(67.7)	23.6(23.5)	24.6(24.2)	24.8(24.3)	23.6(23.6)
$CO_2\underline{Me}$	51.3(51.4)	51.6(51.3)	50.6(50.2)	51.5(51.3)	51.9(52.0)	—	—
$CO\underline{Me}$	(21.2)	(20.8) (21.1)	(20.9) (21.2)	(20.9)	(20.9) (21.9)	(20.9) (21.2) (21.2)	(20.9) (20.9) (21.2)
$\underline{C}OMe$	(170.5)	(170.1) (170.5)	(170.6) (170.9)	(169.8)	(169.6) (170.0)	(170.0) (170.7) (170.7)	(170.4) (170.7) (171.1)

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[a] ^{13}C FT NMR spectra were taken with a Varian NV-14 FT NMR spectrometer at 15.1 MHz with TMS as internal reference (δ_C 0); precision of δ_C are about ±0.1 ppm. [b] Assignments may be reversed.

[c] Dissolved by adding a small amount of CD_3OD.

During the course of this investigation, we have found in SFORD experiments that indirect $^{13}C,^1H$ spin coupling are sometimes very useful for assigning some quaternary carbon signals, as suggested previously.[6] In SFORD experiments, we doubly irradiate the ^1H signal of TMS used as an internal reference, in general. Therefore, residual splittings by indirect $^{13}C,^1H$ couplings can be observed when signals of the respective ^1H

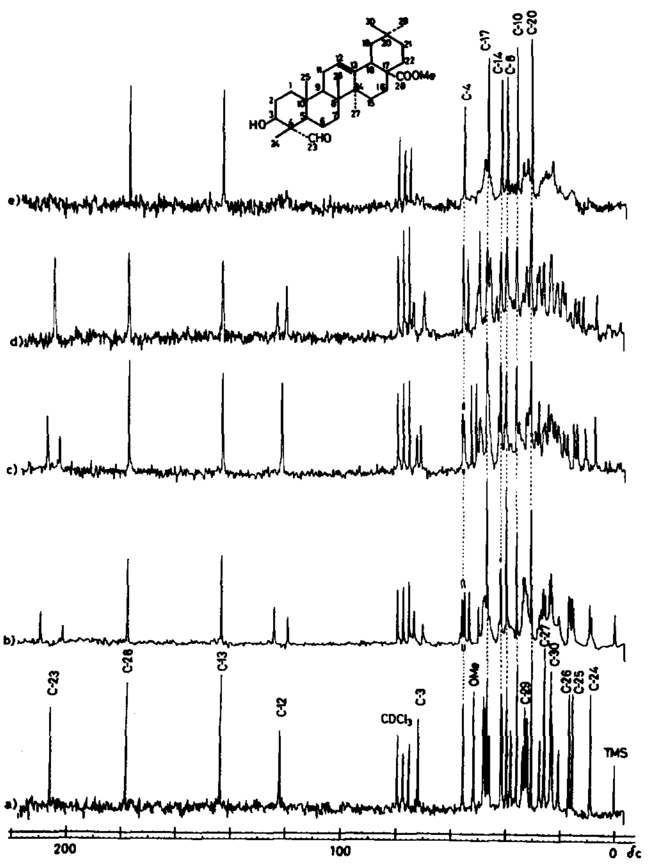

FIGURE. Natural-abundance ^{13}C FT NMR spectra of gypsogenin methyl ester (4) in $CDCl_3$ at 15.1 MHz. (a) ^1H noise-decoupled spectra; (b) SFORD irradiated at 0 Hz [$(C\underline{H}_3)_4Si$]; (c) SFORD irradiated at 317 Hz ($C\underline{H}=C$) downfield from TMS; (d) SFORD irradiated at 563 Hz ($C\underline{H}O$) downfield from TMS; and (e) NORD irradiated at 800 Hz upfield from TMS (at 60 MHz).

coupled strongly to the geminal or vicinal ^{13}C appear at relatively lower fields.[6] The residual splittings of this type were always observed for the quaternary C-14 resonance of all the compounds examined as a distinct doublet in their SFORD spectra, resulting from fairly large H(12)-C(12)=C(13)-C(14) vicinal coupling constants.† Furthermore, we found large splittings of quaternary C-4 signals in SFORD spectra of (4), (5), and their acetates due to large geminal coupling constants (~7 Hz) between the aldehydic proton and C-4. The FIGURE shows various types of ^1H decoupling experiments for (4), for example. We can see the changes in signal shapes of C-4 and C-14 according to the decoupling mode. As can be seen from FIGS. (c) and particularly from (d), irradiation of an ^1H signal at a very low field like a $C\underline{H}O$ signal in an SFORD experiment causes broadenings for most of

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† Incidentally, the C-10 signal will easily be assigned in ^{13}C SFORD spectra of 3-oxo-Δ^4-steroids by this phenomenon.

^{13}C signals owing to residual splittings by many types of indirect $^{13}C,^{1}H$ couplings. However, the doublets due to C-14 and C-4 are clearly seen to collapse into singlets by the selective decouplings, as shown in FIGS. (c) and (d), respectively. Thus, caution must be exercised when quaternary carbon signals are detected by usual SFORD techniques only.

The spectra of all the compounds examined were found to be very much affected probably by the molecular association, as observed for sodium desoxycholate in D_2O.[7] All CH_2 and then CH resonances become substantially broadened as the result of slowing of molecular tumbling and an increasing dipolar-induced relaxation; the CH_3 and especially, quaternary carbon resonances remain rather sharp [see FIG. (a), for example].[7] The trend of broadenings are strengthened by going from a diluted to a concentrated solution, and also from (1) to polyoxy compounds. This phenomenon was of much diagnostic value for determining the number of hydrogens bonded to each carbon in this study, however.

It has also been found that acetylation of a cis-1,3-diol does not shift both α-carbon signals to lower fields, but does to higher fields [see the data on (2), (6), and (7)], and that an introduction of 16-OH [from (4) to (5)] or -OAc considerably shifts the C-9 signal by about -1 ppm by a long-range effect.[8] A further study of the spectra of polyhydroxy compounds including the latter effect is in progress in this laboratory.

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