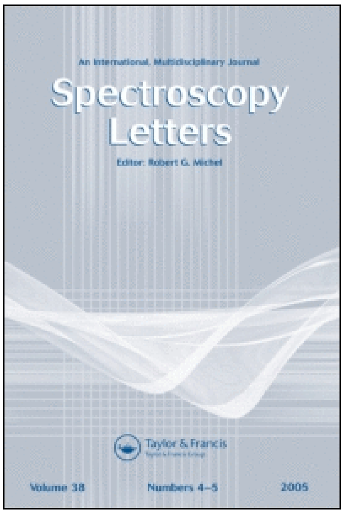

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Carbon-13 Chemical Shift Assignment of β-Cedrene and Some Derivatives

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CARBON-13 CHEMICAL SHIFT ASSIGNMENT OF β-CEDRENE AND SOME DERIVATIVES

Key Words : β-cedrene derivatives, ^{13}C NMR, INADEQUATE, XHCORR, NOESY, Shift reagents

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ABSTRACT: Carbon-13 NMR spectral assignments have been obtained for β-cedrene and three derivatives : β-cedren-9-ol, its acetate and β-cedren-9-one, by combination of two-dimensional NMR techniques and shift reagent experiment.

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INTRODUCTION

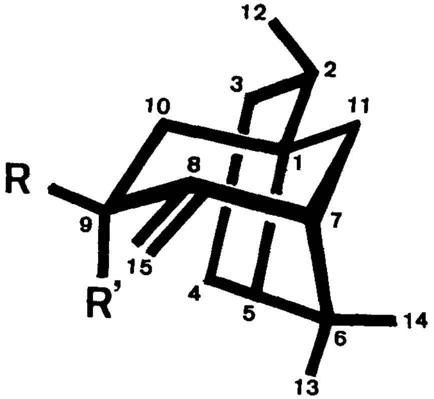
Cedrol, biotol, lac acids and their derivatives bearing the tricyclo[5.3.1.$0^{1,5}$]undecane skeleton are the major or minor constituents of some essential oils (1). A great number of investigations has been done on the synthesis (2), reactivity (3), conformational and spectroscopic analysis (4 - 6) of several of these compounds.

Nevertheless, there are only a few works on spectroscopic data of compounds in these series bearing an exocyclic double bond such as β-cedrene.

In this paper we describe the carbon-13 NMR data, with the unambiguous chemical shift assignment of all carbons, of 8-methylene-2,6,6-trimethyltricyclo[5.3.1.$0^{1,5}$]undecane (β-cedrene) 1, 8-methylene-2,6,6-trimethyltricyclo[5.3.1.$0^{1,5}$]undecan-9-ol (β-cedren-9-ol) 2, its acetate 3 and 8-methylene-2,6,6-trimethyltricyclo[5.3.1.$0^{1,5}$]undecan-9-one (β-cedren-9-one) 4 (FIG. 1).

In the semi-rigid tricyclic framework of the cedrane derivatives, it has been shown that a subtle change of the conformation, induced for instance by the introduction of a substituent with a precise stereochemistry, should provoque an important modification of the carbon chemical shifts (6).

As a consequence, the chemical shifts of most aliphatic carbons of molecules 1-4 are too close to allow an unambiguous assignment based on signal multiplicity and on the analysis of substituent induced steric and electronic effects. The presence of a unic vinylic carbon in the tricyclic framework of these molecules disallowed the comparison with model



1 : R = H, R' = H β-cedrene
2 : R = OH, R' = H β-cedren-9-ol
3 : R = OAc, R' = H β-cedrenyl acetate
4 : R, R' = O β-cedren-9-one

FIG. 1 Structure of β-cedrene and its derivatives.

compounds such as cedrol or 9-cedranol in one hand (no vinylic carbon) and α-cedrene in the other (two vinylic carbons).

EXPERIMENTAL

β-cedrene, β-cedren-9-ol and α-cedrene were purchased from Fluka. Shift reagent Yb(fod)$_3$ was procured from SST. The acetylation (Ac_2O/Py) and oxydation (MnO_2/$CHCl_3$) of 2 led respectively to 3 and 4 with fairly good yields.

β-cedrenyl acetate 3. A solution of β-cedren-9-ol (145 mg, 0.66 mmol) in pyridine (2 mL) and acetic anhydride (2 mL) was stirred overnight at room temperature to allow complete elimination of the alcohol. The reaction mixture was extracted by ether. The combined organic layer was washed with saturated $CuSO_4$ solution, saturated Na_2CO_3 solution, water, and dried over $MgSO_4$. The solvent was removed under reduced pressure (yield : 75%).

β-cedren-9-one 4. A solution of β-cedren-9-ol (110 mg, 0.5 mmol) in chloroform (5 mL) and manganese oxide (410 mg, 5 mmol) was stirred overnight at room temperature. After filtration, the organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure (yield: 95%).

All NMR spectra were recorded on a Bruker WP 200 SY Fourier transform spectrometer operating at 200.132 MHz for ^{1}H and 50.323 MHz for ^{13}C in deuteriated chloroform (1D NMR, XHCORR, NOESY) or hexadeuteriated benzene (INADEQUATE), with all shifts referenced to internal tetramethylsilane (TMS). Carbon and proton NMR spectra were recorded respectively with the following parameters : pulse width (PW) : 3.2 μs (flip angle 45°) and 2 μs (flip angle 25°) ; acquisition time : 1.3 and 2.3 s for 32 and 16K data table with spectral widths (SW) of 250 and 13 ppm. Carbon-13 spectra were recorded with broad band decoupling and a digital resolution of 0.763 Hz/pt. Exponential multiplication of the free induction decay (FID) with a line broadening of 1.0 Hz was used before Fourier transformation.

The following parameters were used for spin-echo experiments (JMODXH Bruker microprogram) : PW (90°) : 6.4 μs ; relaxation delay (RD) : 4 s ; 1/J(C,H) delay = 7.0 ms ; SW : 12500 Hz.

The proton-carbon chemical shift correlation utilized the XHCORR sequence with delays optimized for J(C,H) values of 140 Hz. The spectra were acquired with 2K x 256 data points and a data acquisition of 64 x 256 increments in t_1 and a zero filling in the F_1 dimension. The correlation experiments were applied using various F_2 spectral widths ranging from 4 to 7 kHz. The proton F_1 spectral width was 1200 Hz. The fixed delays were a 5 s relaxation delay, 4.0 ms polarization transfer delay and 2.0 ms refocusing delay. A 5 s delay was used between pulse for each value of t_1, 256 transients were accumulated. The data were processed with a unshifted sine bell window fonction in each dimension.

The 2D NOESY spectra were performed using 256 t_1 and 1K t_2 points. The mixing time was 1.5 s. The time domain data were zero filled to 512 points along the t_1 axis. The data were multiplicated by sine bell window fonctions along the t_2 and t_1 axis prior to respective Fourier transformations.

The carbon-carbon correlated 2D spectrum (INAD2D) was acquired with a spectral width of 7100 Hz in the F_2 domain and a 32-step phase cycling and data acquisition of 128 x 256 increments of t_1 to provide, after zero filling in the F_1 dimension, a matrix of 2048 x 512. Data files were processed using unshifted sine-bell squared function in both dimensions prior to Fourier transformation. The delay for the creation of double quantum coherence was 6.5 ms and the relaxation delay was 10 s.

RESULTS AND DISCUSSION

The unambiguous chemical shift assignment of all carbons (excepted C13 and C14) of β-cedrene 1 has been achieved by two dimensional carbon-carbon connectivity experiment (INADEQUATE) (Table 1, FIG.2 shows the upfield region).

The chemical shift assignment of most carbons of 2 and 3 is straightforward using compound 1 as model and taking into account the α and β effects of hydroxy or acetoxy group. The C10 and C11 resonances of alcohol 2 are differenciated by shift reagent experiment. It is

TABLE 1
Carbon Chemical Shift Assignment of Compounds 1-4 and α-Cedrene 5

	1	2	3	4	5
1	54.42	54.92	54.67	54.38	53.87
2	42.18	41.68	41.81	41.84	41.55
3	37.07	36.76	36.84	36.64	36.15
4	25.73	25.88	25.93	25.70	24.83
5	56.50	57.08	56.99	59.23	59.06
6	42.31	42.30	42.27	43.50	48.14
7	60.79	60.42	60.63	57.86	54.94
8	151.70	154.14	148.77	148.61	140.50
9	29.76	70.13	71.87	201.58	119.24
10	33.70	44.95	40.59	51.56	38.84
11	45.09	45.01	44.72	42.41	40.69
12	15.37	15.50	15.45	15.39	15.42
13	25.90	26.16	26.29	28.63	27.66
14	26.62	26.72	26.68	25.88	25.62
15	107.60	106.56	106.92	120.81	24.73
CH_3			21.14		
C = O			170.43		

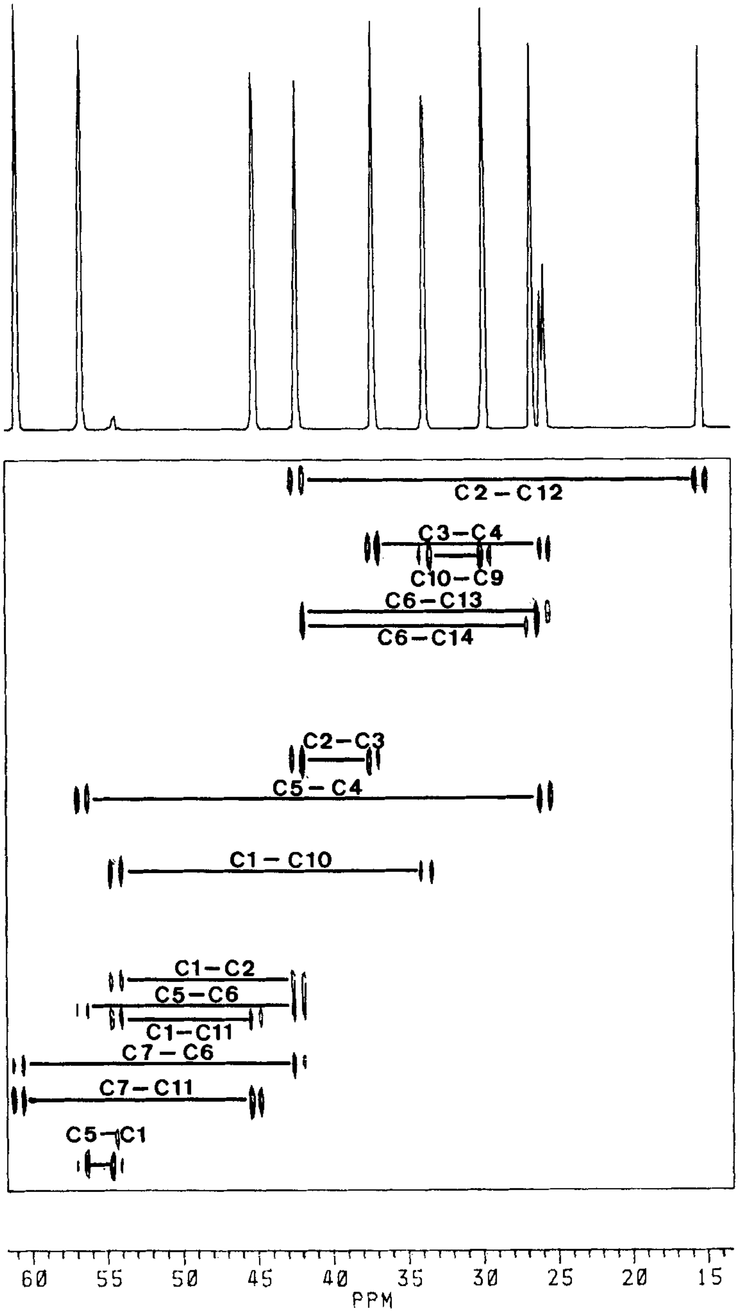


FIG. 2 2D INADEQUATE Spectrum of β-cedrene 1 (upfield region).

note worthy that for compounds 2 and 3, the chemical shift values of brigdehead carbons C5 on one hand and C7 on the other are very close to those of β-cedrene and could be assigned by comparison. For these three compounds, the XHCORR spectra allowed the identification of the hydrogens bonded to these carbons and showed that they have the same multiplicities ie a triplet for H5 and a doublet for H7.

The introduction of a carbonyl function (ketone 4) in the tricyclic framework led to the expected chemical shift variations on the neighbouring carbons. The C5 and C7 carbons were assigned through their correlations in the XHCORR spectrum with the hydrogens H5 and H7 identified on the basis of the similarity of their multiplicity over all the series (triplet for H5 and doublet for H7).

At this stage, the only remaining ambiguity concerned the assignment of chemical shifts of C13 and C14. On α-cedrene and isocedrol, the carbons C13 and C14 have been differenciated unambiguously by selective deuteriation of methyle C13 which needed an eight steps synthesis (5). For compounds 1-4 we choose another strategy based on a combination of two dimensional NMR techniques : proton-carbon (XHCORR) and proton-proton (NOESY) correlation experiments. This procedure, which is described below, was checked on α-cedrene 5 (the results fitted perfectly with the litterature) (5) and then applied to β-cedrene and its derivatives.

Concerning α-cedrene, all the carbons have been assigned unambiguously (carbon-carbon correlation and deuteriation) as well as the hydrogens bonded to each of them (heteronuclear correlation) (5). This allowed us to observe, on the NOESY spectrum of α-cedrene, an interaction between the bridgehead hydrogen H7 and methylic hydrogens H14. This interaction could be used as a probe on compounds 1-4 for the differenciation of hydrogens H13 and H14 and then of carbons C13 and C14, through XHCORR experiment.

For the parent hydrocarbon β-cedrene, the proton-carbon correlation allowed the identification of hydrogens H5 (triplet at 1.80 ppm), H7 (doublet at 2.18 ppm) and H9 (multiplet at 2.35 ppm) bonded respectively to carbons which resonate at 56.50, 60.79 and 29.76 ppm. The homonuclear proton-proton correlation experiment (NOESY spectrum) showed one interaction between H7 with protons which resonate at 0.97 ppm. As a consequence this signal is assigned to hydrogens H14. Coming back to XHCORR spectrum allowed the assignment of C14 at 26.62 ppm. Incidently, one could observe in the NOESY spectrum, another interaction between hydrogen H9 endo and protons which resonate at 0.95 ppm, bonded to the carbon at 25.90 ppm, thus confirmed as C13.

The same procedure was then applied to 2, 3 and 4. For the latter, a complementary interaction between H5 and H13 was observed on the NOESY spectrum.

These results confirmed that the number of ethylenic carbons present into the tricyclic cedrane skeleton has a strong influence on the chemical shift of most carbons.

Large differences on chemical shifts of several carbons of β-cedrene are observed by comparison with α-cedrene : C6 (-5.8 ppm), C7 (+5.8 ppm), C10 (-5.1 ppm) and C11 (+4.4 ppm), wich implies that these two olefines have different conformations of the six membered ring :

probably a flat chair for α-cedrene and a "boat" for β-cedrene, as it could be expected by the 6 ppm shielding of carbon C6 and by analogy with cedrol oxyde (6).

It is noticeable that the carbon chemical shifts values has to be inverted for C5 and C7 as well as C13 and C14 in β-cedrene comparatively to α-cedrene.

The chemical shifts of compounds 1-3 are very similar for most carbons, excepted for those which are close to the substituent. It could be assumed that the presence of hydroxy or acetoxy group does not introduce any modification of the conformation. Conversely, larges differences are observed for the chemical shifts of several carbons of the bicyclo [3.2.1] octane substructure of cedrenone comparatively to α-cedrene as well as β-cedrene. Nevertheless, one could observe that carbons C5 and C7 in one hand, carbons C13 and C14 in the other, display the same order than they do in α-cedrene.

CONCLUSION

In this study, the combination of two dimensional NMR techniques allowed the chemical shift assignment of all carbons of β-cedrene and three derivatives. Evidently, α and β-cedrene don't adopt the same conformation. The introduction of a monovalent oxygenated function on C9 affect only the neighbouring carbons. The study of β-cedren-9-one has to be achieved independantly without comparison neither with β-cedrene nor with α-cedrene.

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