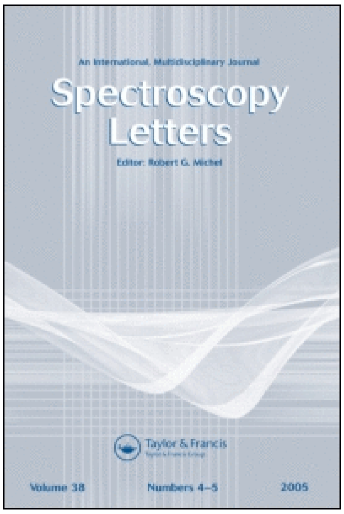

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2D NMR STUDY OF PHOTOTETRAHYDRO ZEXBREVIN A

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ABSTRACT

The homo and hetero correlated 2D experiments on the title product have led to the unambiguous assignment of proton and carbon NMR spectra.

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The study of the photochemical behaviour of germacranolides has attracted the attention of several groups.[1-3] The structures of photoproducts obtained in this reaction depend on the conformation of the starting material.[2]

Zexbrevin 1, a heliangolide (E,Z germacranolide) isolated from Zexmenia brevifolia,[4] contains a 3(2H)-furanone moiety which confers a high degree of conformational rigidity on the molecule.

Photolysis of a methanolic solution of tetrahydrozexbrevin 2 yielded three photoproducts whose structures were determined by chemical and spectroscopic means and confirmed by X-ray diffraction analysis.[5]

The assignment of the ^{1}H NMR spectra of photoproducts A, B and C was made using the double resonance technique. We performed two sets of 2D NMR experiments on the photo tetrahydro zexbrevin A(3) in order to confirm the previous assignments:[5]

i) ^{1}H ^{1}H homonuclear correlation (COSY HOMO)

and ii) ^{1}H ^{13}C heteronuclear correlation (HETERO).

Given the importance of this tetracyclic system to further studies of photoproducts from the same plant, as well as the unique character of the structure, it was necessary to obtain a reliable set of spectral data. The two techniques enabled us to realize these objectives completely.

i) ^{1}H ^{1}H Homonuclear Correlated Spectra of Phototetrahydro Zexbrevin A(3)

The highly rigid structure of this molecule is one cause of difficulty in assignment of protons (Fig. 1). Five methyl signals lie very close to each other, the three methylenes (C-2, C-9 and C-5) form an interesting coupling series, and of five methine protons only the isopropyl one could be unambiguously assigned from the one-dimensional NMR spectrum. Table 1 shows the assignment using high resolution 500 MHz spectra as confirmed by a COSY

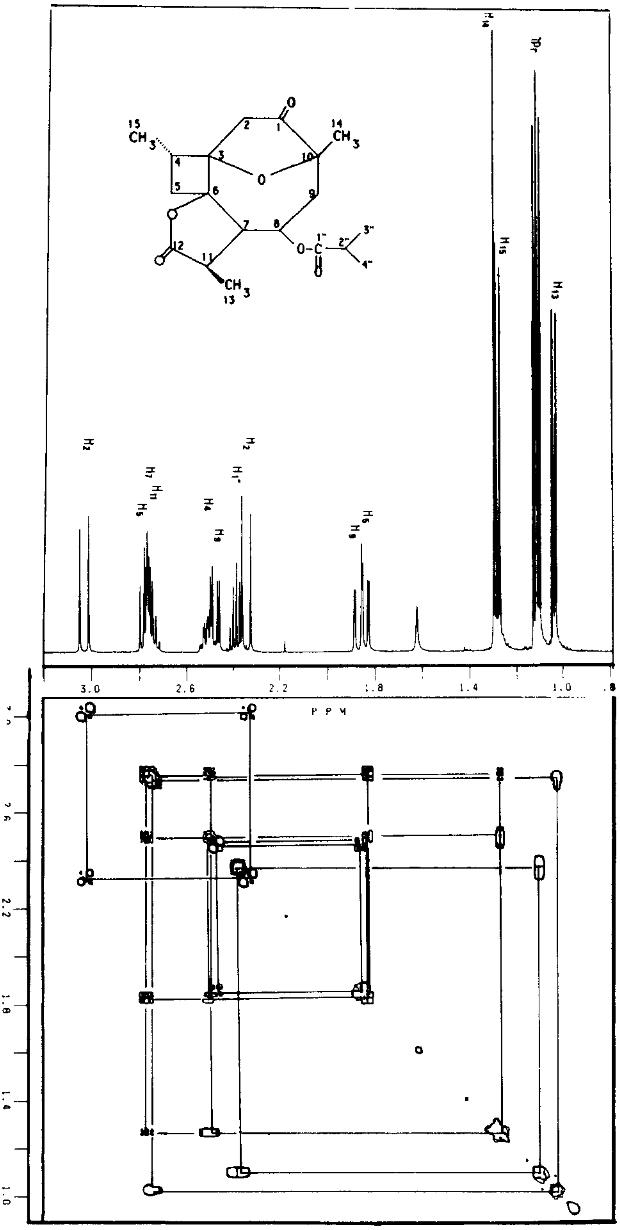

Fig. 1 Compound 3: proton two dimensional homonuclear chemical shift correlated spectrum (COSY): off diagonal contours of intensity indicated spin coupling between protons at chemical shifts given by two coordinates. The one dimensional 500 MHz spectrum is represented by contours along the diagonal (+30°, $CDCl_3$).

Table 1

High resolution ^{1}H and ^{13}C NMR spectra of 3. Chemical shifts assignment.

Carbon	δc	Proton	δH	multiplet	(JHz)*
C-1	215.0	-	-		
C-2	37.6	H-2	3.05	d	(19.0)
		H-2'	2.35	d	(19.0)
C-3	88.5	-	-		
C-4	35.1	H-4	2.52	m	(2.5, 7.5, 9.0)
C-5	39.2	H-5	2.78	dd	(9.0, 12.5)
		H-5'	1.83	dd	(2.5, 12.5)
C-6	83.0	-	-		
C-7	49.8	H-7	2.78	dd	(8.0, 1.0)
C-8	69.2	H-8	4.96	ddd	(1.0, 2.5, 4.2)
C-9	42.8	H-9	2.48	dd	(4.2, 15.5)
		H-9'	1.88	dd	(2.5, 15.5)
C-10	89.4	-	-		
C-11	36.6	H-11	2.75	m	(8.0, 6.5)
C-12	177.2	-			
C-13	8.8	H-13	1.03	d	(6.5)
C-14	24.4	H-14	1.29	s	
C-15	15.7	H-15	1.28	d	(7.5)
C-1"	175.7	-			
C-2"	33.9	H-2"	2.38	sept	(7.0)
C-3"	18.0	H-3"	1.11	d	(7.0)
C-4"	18.4	H-4"	1.12	d	(7.0)

* s - singlet, d - doublet, sept - septet, m - multiplet

experiment. The methylene protons display three AB patterns with the $\Delta\delta$ varying from 0.7 ppm (δ 3.05 and 2.35) for α-to carbonyl protons at C-2 to 0.95 ppm (δ 1.83 and 2.78) for cyclobutane-ring protons at C-5.

The COSY experiments clearly show several sequences of couplings: for the cyclobutane ring; for protons at C-9, C-8, C-7, C-11 and C-13; for iso propyl and the above-mentioned furan methylene.

Several long range couplings have been detected and confirmed by COSY experiments. For instance as the starting point of two analysis, the C-15 methyl protons (1.28) and H-5 (at 2.78) are showing the long range coupling of 3H2. The X-ray crystallography (5) shows that C-15 methyl proton and H-5 are synperiplanar, and consequently a long range coupling is observed. The small coupling between H-4 and H-5 of 2.5 Hz confirms this assumption.

The H-2 and H-2^1 (at 2.35 and 3.05 respectively) correlate strongly, the signal of H-5 (2.78) correlates with H-4 and H-5^1 (2.52 and 1.83) as well as with methyl H-15. Finally a strong correlation of H-11 and methyl H-13 protons have been observed.

The COSY experiment generally confirms the assignment proposed and permits the completion of the structural analysis with conformational preference and precise assignment of protons. In particular the previous assignment of the 2.75 - 2.78 area containing three protons has been corrected (Table 1).

ii) ^{1}H ^{13}C Heteronuclear Correlated Spectra of 3

The exact assignment of carbon signals in the C-13 spectrum of 3 has been performed using 2D experiments as well as off-resonance spectra.

The 2D (Figure 2) heterocorrelated spectra recorded in $CDCl_3$ enables us to assign all protons bound to carbon and to correct the identification previously proposed.

The coaxial display of reference proton spectrum is made in order to enable easier identification of signals and to check the correlation in highly crowded areas. The carbon spectrum is shown separately (Figure 3) together with appropriate off-resonance notations.

Three quarternary carbons as well as three carbonyl signals have been identified from both INEPT and long range coupling experiments. As for the five methine carbon signals, the most difficult to assign were C-4 at 35.7 and

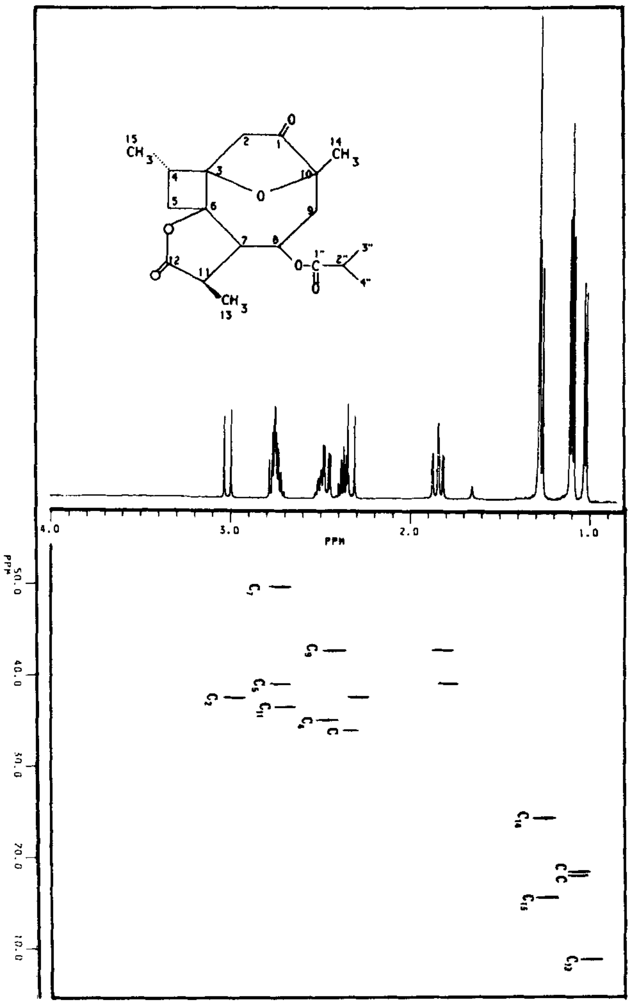

Fig. 2 Compound 3: proton carbon two dimensional heteronuclear chemical shift correlated spectrum (Hetero). The reference proton 500 MHz spectrum is shown on the axis (+30°, $CDCl_3$).

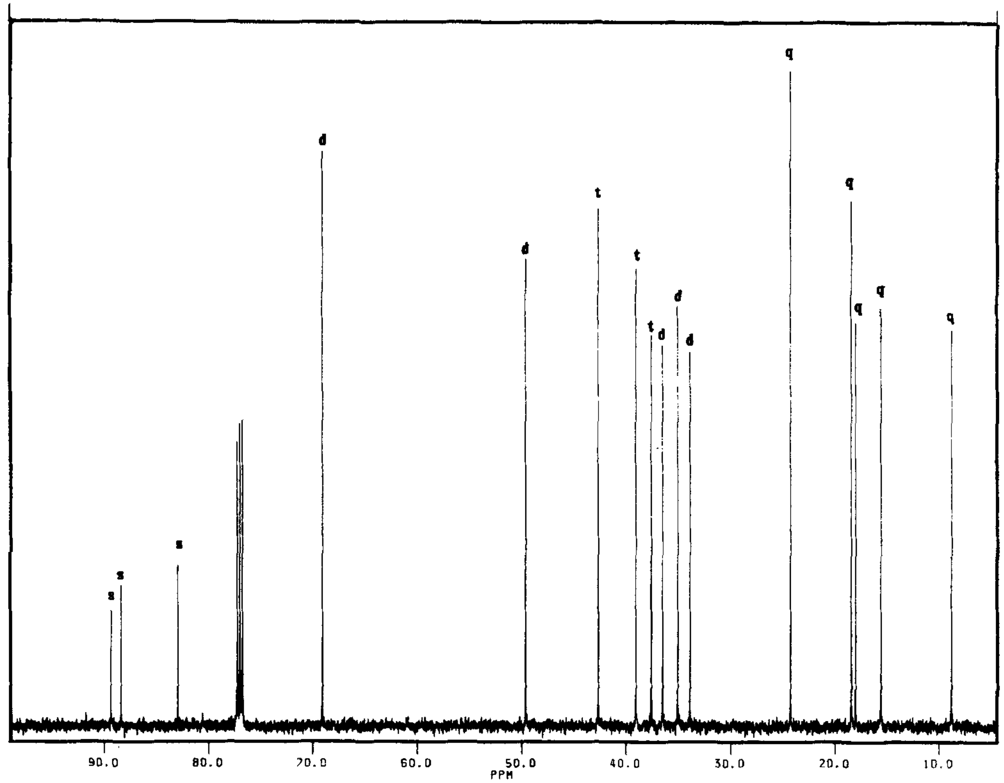

Fig. 3 Reference carbon 125 MHz spectrum of 3.

C-11 at 38.5. In spite of the ~3 ppm separation of these signals and the difference in chemical environment, the correct identification was made only after the correlation with the COSY spectrum previously reported. The remaining three methines were identified (isopropyl, C-8 and C-7) much more easily.

Three methylene carbons signals lie within a 5 ppm range. Their correct assignment follows from the 2D correlation spectrum. The most hindered belongs to methylene at C-2 (at 37.6 ppm). Two lower field methylenes, which were also previously wrongly assigned, have been interchanged: the signal at δ 39.0 ppm belongs to the C-5 and that at 42.6 to the C-9 methylene carbon.

The assignment of the three ring methyls was facilitated by 2D experiments, the most upfield signal belonging to the lactonic α-to carbonyl methyl. The methyl on the cyclobutyl ring as well as the angular methyl C-14 and the isopropyl methyls display the characteristic chemical shifts. Table 1 contains the correct final assignment of all carbons of phototetrahydro zexbrevin A(3).

Experimental

All experiments were performed on samples of 3 of variable weight as c.a. 10% $CDCl_3$ solutions in 10 mm sample tubes for ^{13}C and 5 mm tubes for ^{1}H (0,5 ml of solution used). All chemical shifts are expressed in δ(ppm) using TMS as internal standard. Coupling constants are expressed in Hz. The spectrometers were locked on the deuterium signal of the solvents. The 2D experiments together with other spectral identifications have been performed on Bruker AM-500 operating as 500 MHz for H-1 and 125.7 for C-13 and on Bruker WM 360.

Bruker Spectrometer was equipped with an Aspect 2000 computer, operating in the Fourier Transform mode. Without other specification, typical one dimensional spectral acquisition parameters were: spectral width 4000 Hz, pulse width 4 μs (90° = 7.5 μs) and 16384 time domain addresses. Acquisition time was 2.048s. No relaxation delay was used. Processing was also made with 16384 addresses (accuracy 0.488 Hz).

Two dimensional homonuclear correlated (COSY) spectra were recorded using the pulse sequence (D_1 -90° - D_2 -45° $-D_3$)n where D_2 and D_3 are the evolution and observation periods respectively. Spectra were recorded with 256 increments of D_2 from 0.003 ms to 128 ms. Acquisition time D_3 was 0.512 s for 2000 Hz of spectral width. Data were acquired in 2048 addresses at each D_2 value with the carrier in the center of the spectra. For 64 scans at each D_2 all data acquisitions time is 7.45 hours with D_1 = 1 s. Processing was performed with 2048 addresses in F_2 and 1024 addresses in F_1 domains. Prior to Fourier transform Free induction decay were multiplied by a non shifted sine bell window function in both domains.

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