

NEW ^{13}C -NMR TECHNIQUES APPLIED TO PENTALENOLACTONE STRUCTURE

Setsuo Takeuchi*, Jun Uzawa, Haruo Seto† and Hiroshi Yonehara†

The Institute of Physical and Chemical Research, Wako-shi Saitama, 351 Japan

† Institute of Applied Microbiology, The University of Tokyo, Tokyo, 113 Japan

(Received in Japan 14 May 1977; received in UK for publication 5 July 1977)

An exhaustive ^{13}C -NMR analysis of the unique structure of pentalenolactone^{1,2} was carried out on its methyl ester, using precisely determined ^1H -NMR frequencies for single-frequency $^{13}\text{C}\{-^1\text{H}\}$ of direct as well as long-range couplings, and besides, for selective $^{13}\text{C}\{-^1\text{H}\}$ NOE. These were made possible by using a JEOL FX-60 FT-NMR spectrometer equipped with a dual $^{13}\text{C}/^1\text{H}$ probe, which enabled to carry out well-tuned decoupling experiments immediately following the precise reading of ^1H signal frequencies, only by simple switch operations. In this work, the methyl ester contained in a degassed and sealed 10mm tube as a CDCl_3 solution (20%). ^1H Chemical shifts are recorded in Table I.

Table I. ^1H Chemical Shifts (60 MHz, CDCl_3) of Pentalenolactone, which were used as a Guide in Selective $^{13}\text{C}\{-^1\text{H}\}$

	H1	H3	H5	H7	H8	H10	H12	H14	H15	H13'
δH (ppm)	2.85	5.12	a	6.82	3.44	2.76 3.24 ^a	4.64	1.04	1.66	3.79

a Overlapped with the H10 signal at almost the same chemical shift.

The ^{13}C -NMR spectra with ^1H noise decoupling (PND) and in the "Gated-1" spin-decoupling mode (that means without ^1H decoupling with NOE) are shown in Figs. 1A and 1B, respectively. The signals (Fig. 1B), i.e., 3 quartets, 2 triplets, 5 doublets, and 6 singlets, are in accord with the structure of pentalenolactone.

Further confirmations of carbon signal assignments were made by an application of selective ^1H decoupling experiments. For the examination of $^{13}\text{C}\{-^1\text{H}\}$

of direct couplings, each proton signal was selectively irradiated with a weak power of single frequency (ca. 0.4-0.5 gauss), successively. This experiment gave the ^{13}C signal assignments as shown in Table II except for the quaternary carbons.

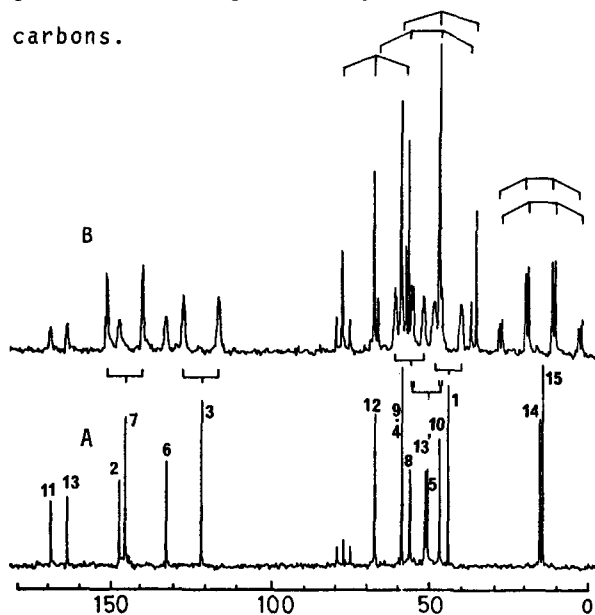


Fig. 1. ^{13}C -NMR Spectra of pentalenolactone at 15.05 MHz in CDCl_3 (temp. 27°C , pulse angle 45° , repetition time 2 sec, spectral width 4 KHz); A: PND spectrum (200 scans); B: "Gated-1" spectrum (8000 scans).

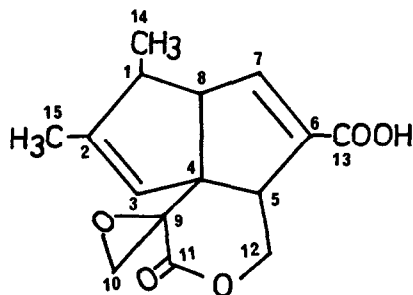


Fig. 2. Structure of pentalenolactone

Long-range $^{13}\text{C}-^1\text{H}$ coupling was evidenced by single-frequency ^1H irradiation of the interacting proton signal by weak appropriate power (ca. 7-10 mgauss), which was found by the calculation by using the following equation³:

$$H_2 = J(\gamma_{\text{H}}^2 - \gamma_{\text{C}}^2)^{1/2} / 2\gamma_{\text{H}}\gamma_{\text{C}} = 0.452 \text{ (mgauss/Hz)}J$$

This irradiation eliminated fine splittings due to a long-range $^{13}\text{C}-^1\text{H}$ coupling, leaving a simplified or a better defined signal due to the direct $^{13}\text{C}-^1\text{H}$ coupling. For example, in Fig. 3A which shows an expanded portion of the "Gated-1" spectrum, the C5 signal ($\delta 51.0$) is a doublet further split by a long-range coupling. Irradiation at the frequency of H7 ($\delta 6.8$) eliminated the fine splitting of C5, retaining a doublet due to the direct $^{13}\text{C}-^1\text{H}$ coupling (see Fig. 3B).

Although the two quaternary C4 and C9 atoms are apparently in different

environmental conditions, they were found to give practically identical chemical-shifts and relaxation-times (T_1) as seen from Table II. Individual assignments for these carbons, however, was made possible by the selective long-range $^{13}\text{C}-\{^1\text{H}\}$ at the frequency of H3 ($\delta 5.12$) or H10 ($\delta 3.24$). Thus, all the signals were assigned to the respective carbon atoms in pentalenolactone, as summarized in Table II, and the general scheme of the decoupling experiments is shown in Fig. 4.

It should be emphasized that the long-range $^{13}\text{C}-\{^1\text{H}\}$ technique employed here enabled (1) the reliable assignment of a carbon atom with a two or three bond-coupling to proton, (2) the direct assignment of a carbon atom having no attached proton, and (3) the examination of long-range couplings via an ester bond.

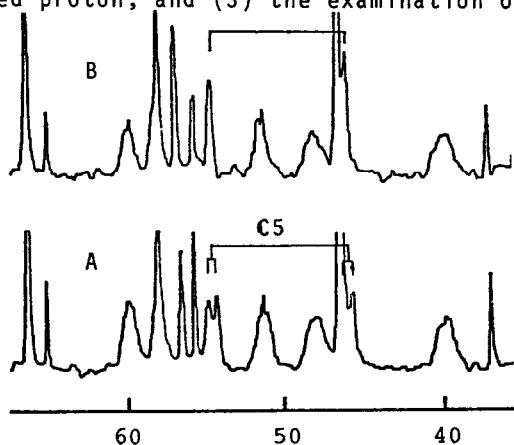


Fig. 3. Selective long-range $^{13}\text{C}-\{^1\text{H}\}$ of C5, irradiated H7; A: "Gated-1" spectrum; B: H7 irrad. spectrum

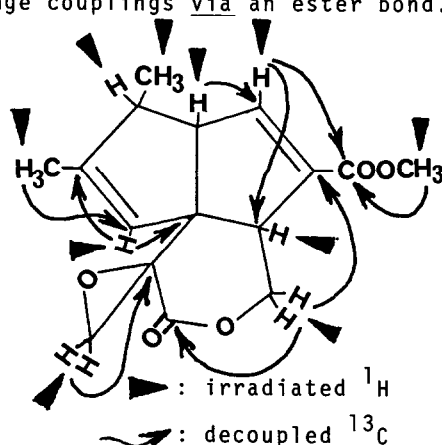


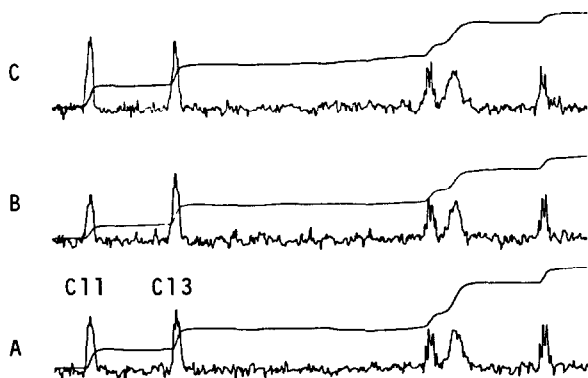
Fig. 4. Experimental scheme of selective $^{13}\text{C}-\{^1\text{H}\}$

Table II. ^{13}C Chemical Shifts and Relaxation Times of Pentalenolactone

	C1	C2	C3	C4	C5	C6	C7	C8	C9
δC (ppm)	44.5	147.9	122.3	59.2	51.0	133.4	146.1	56.7	59.1
T_1 (sec)	1.1	16	1.4	23	1.3	26	1.1	1.4	23
	C10	C11	C12	C13	C13'	C14	C15		
δC (ppm)	47.1	169.4	67.7	164.3	51.8	15.5	14.6		
T_1 (sec)	0.7	57	0.68	49	3.7	0.66	2.3		

Reference standard: center of CDCl_3 = 77.25 ppm = 1161 Hz TMS at 15.05 MHz.

During the decoupling studies, frequent observations suggested the possibility of an application of selective $^{13}\text{C}-\{^1\text{H}\}$ NOE by selective ^1H saturation for more reliable structural elucidation of complex molecules. In fact, enhancements of ^{13}C signals without elimination of splittings were actually observed: i.e., that of the C13 signal by irradiation of the H5, H7, or H12 signal with a weak power (6 mgauss): and that of the C11 signal by irradiation of the H10 or H12 signal (see Fig. 5).



The technique of the selective $^{13}\text{C}-\{^1\text{H}\}$ NOE as well as the long-range $^{13}\text{C}-\{^1\text{H}\}$ by single-frequency irradiation, should promise the future application.

Technical details of these experiments will be reported elsewhere.

Fig. 5. Selective $^{13}\text{C}-\{^1\text{H}\}$ NOE; A: non decoupled spectrum; B: irradiated at H7; C: irradiated at H12.

REFERENCES

- (1) S. Takeuchi, Y. Ogawa and H. Yonehara, *Tetrahedron Letters*, 2737 (1969)
- (2) D. G. Martin, G. Slomp, S. Mizsak, D. L. Duchamp and C. G. Childester, *Tetrahedron Letters*, 4901 (1970)
- (3) E. G. Paul and D. M. Grant, *J. Am. Chem. Soc.*, **86**, 2977 (1964)