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LONGITUDINAL RELAXATION TIMES AND STRUCTURE ELUCIDATION—I

FATTY ACIDS AND ESTERS

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Abstract—The ^{13}C relaxation times fo several fatty acids and esters were measured. The values obtained can be used for assigning the carbon resonances or for locating the double bond along an alkyl chain.

Until recently, nuclear magnetic resonance provided the organic chemist with two kinds of data; chemical shifts and integrated intensities. To a lesser extent, information could be gained from linewidths. Fourier transform spectrometers brought a new kind of data within reach of the organic chemist: relaxation times. This is especially easy to obtain in ^{13}C NMR where, under incoherent proton irradiation, the absence of couplings allows pure exponential relaxation, yielding a single relaxation time[1] which can be related[2] to the correlation time and the C–H bond length.

If a carbon bears n hydrogen atoms the effects are additive and nT_1's must be considered. If it is assumed that the C–H bonds have the same length for all organic molecules, the nT_1's are then a direct measurement of the correlation times.

This paper will show how the T_1's can be used for signal assignments and structure elucidation in molecules presenting great motional anisotropy.

It has been observed that the relaxation times of carbons increased along an alkyl chain if one end is "anchored" in the solvent.[3] Theory predicts this increase to be exponential.[4] Little is known if the chain contains one or more double bonds. Therefore, in order to test if the general rules for long chain alkanes still apply when the chain is more or less perturbed, a series of unsaturated fatty acids was studied.

RESULTS AND DISCUSSION

Such compounds have already been subjected to several ^{13}C investigations[5–7] and the assignment of their resonances presented little difficulties. In the present study, special attention was paid to the methylene carbon area around 29 ppm, in order to resolve the maximum number of lines. All the results are condensed in Fig. 1. Such a presentation shows more clearly the compounds with their chemical shifts and T_1's than when separated.

In the case of undecenoic acid **1**, five carbon atoms were immediately located, the four remaining carbon atoms appearing as 3 peaks, one of tem (28.82 ppm) being twice as large as the others. Although the individual signals were not assigned for carbon atoms 4–7, these atoms have T_1's shorter than C-8 but longer than C-3.

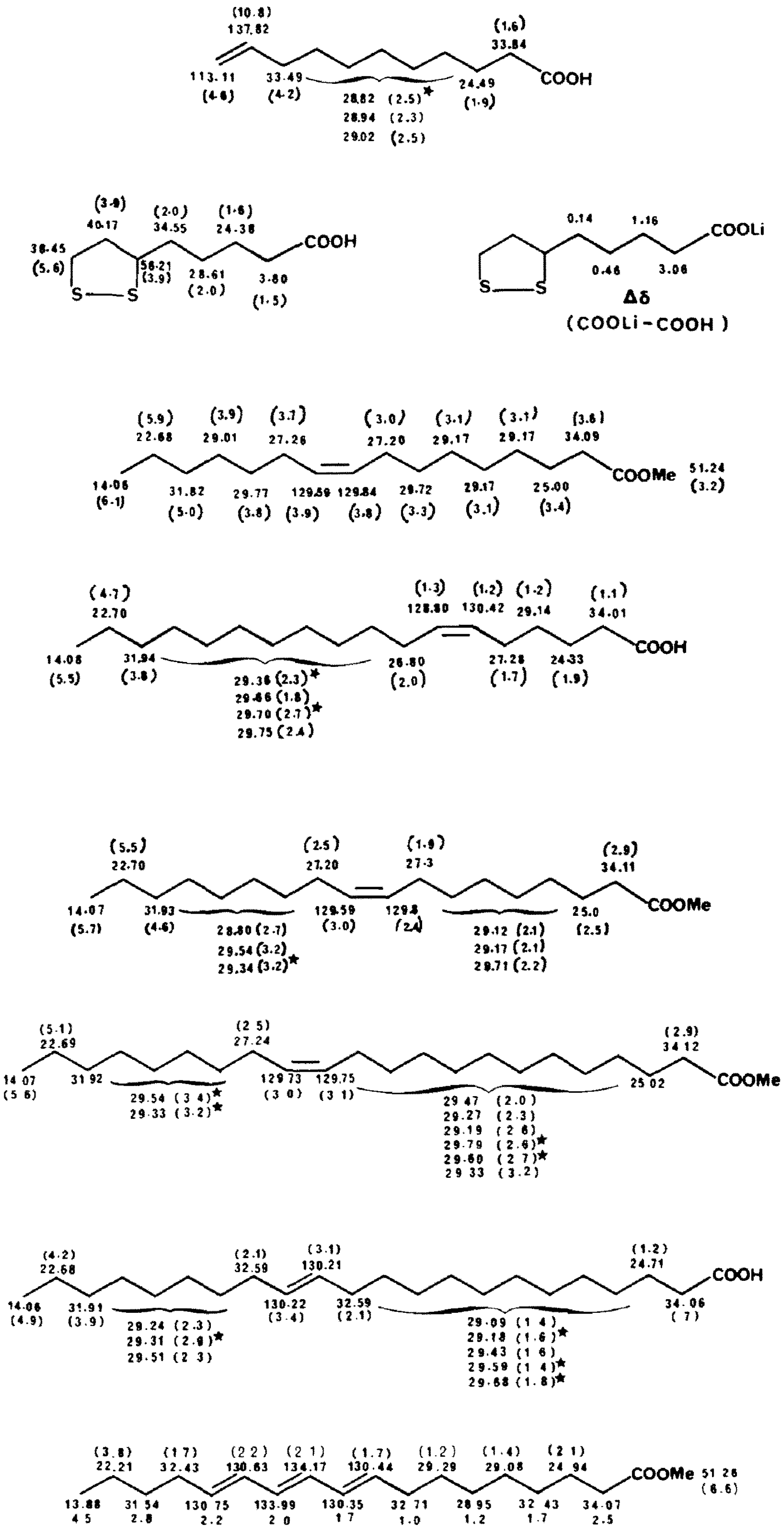
The nT_1's of carbon atoms 10 and 11 did not appear in the anticipated order. It will be seen in the case of poly-unsaturated compounds that this effect is general.

In α-lipoic acid **2** the end of the chain is perturbed by a heterocycle. The carbon resonances were assigned by recording the spectrum of the lithium salt. This was simply done by adding $LiCO_3$ to the solution of the acid. Here again, the T_1's increased along the chain and *also on the ring.*

In order to test the effect of the position of the double bond along the chain, three C_{18} compounds were studied. Palmitoleic acid methyl ester **3**, petroselinic acid **4**, oleic acid methyl ester **5**. The presence of different carboxyl function at the end of the chain allows the study of the effect of the terminal group. Furthermore, the compounds were commercially available. In all these cases, the individual carbon resonances were not completely resolved. Nevertheless the three terminal carbons (δ 14.0, 22.7 and 31.9 ppm), the two carbons adjacent to the double bond (δ 27.2 ppm) and carbon atoms 2 and 3 (δ 34.0 and 25.0 ppm) could always be assigned. This gave T_1 values at the end, the middle and the beginning of the chain. As shown in Fig. 1, the remaining resonances had T_1 values which were ranging in the intervals left. In contrast to the case of the acid compounds both methyl esters **3** and **5** presented T_1 values increasing towards both ends of the chain. The minimum value of the relaxation times was located three or four atoms away from the carboxyl function. This is dependent on the size of the ester group, as shown by the ethyl ester **9**, where that minimum was located on the β carbon.

Two longer (C_{22}) compounds were next studied: erucic acid methyl ester **6** and brassidic acid **7**. The latter will be taken as an example. Nine of the twenty two resonances were assigned immediately: the three terminal carbons (14.06, 22.68 and 31.91 ppm), the two carbons adjacent to the double bond (both at 32.59 ppm) and the carbons α and β to the carboxyl function (34.06 and 24.71 ppm). The remaining carbons appeared as shown on Fig. 2. There were only three peaks (four carbons) having T_1's greater than the T_1's of the carbons α to the double bond (2.1 sec). The five other resonances (8 carbons) had T_1's ranging from 1.4 to 1.8 sec. This is in agreement with structure **7**.

The preceding discussion has been restricted to saturated carbons. The T_1's of all the unsaturated carbons in the products studied so far were always too short compared with the nT_1's of the adjacent carbons. The effect of different lengths for alkyl and alkenyl bonds is not sufficient to explain the observed differences. The relaxation rate of nucleus C situated at a distance r from another nucleus H is given in the "extreme narrowing"


(10.8)
137.82
(1.6)
33.84
113.11
(4.6)
33.49
(4.2)
28.82 (2.5)*
28.94 (2.3)
29.02 (2.5)
24.49
(1.9)
COOH
(3.8)
40.17
(2.0)
34.55
(1.6)
24.38
COOH
38.45
(5.6)
56.21
(3.9)
28.61
(2.0)
3.80
(1.5)
S
S
0.14
1.16
COOLi
0.46
3.06
S
S
Δδ
(COOLi−COOH)
(5.9)
22.68
(3.9)
29.01
(3.7)
27.26
(3.0)
27.20
(3.1)
29.17
(3.1)
29.17
(3.6)
34.09
14.06
(6.1)
31.82
(5.0)
29.77
(3.8)
129.59
(3.9)
129.84
(3.8)
29.72
(3.3)
29.17
(3.1)
25.00
(3.4)
COOMe
51.24
(3.2)
(4.7)
22.70
(1.3)
128.80
(1.2)
130.42
(1.2)
29.14
(1.1)
34.01
COOH
14.08
(5.5)
31.94
(3.8)
29.36 (2.3)*
29.66 (1.8)
29.70 (2.7)*
29.75 (2.4)
26.80
(2.0)
27.28
(1.7)
24.33
(1.9)
(5.5)
22.70
(2.5)
27.20
(1.9)
27.3
(2.9)
34.11
14.07
(5.7)
31.93
(4.6)
28.80 (2.7)
29.54 (3.2)
29.34 (3.2)*
129.59
(3.0)
129.8
(2.4)
29.12 (2.1)
29.17 (2.1)
29.71 (2.2)
25.0
(2.5)
COOMe
(5.1)
22.69
(2.5)
27.24
(2.9)
34.12
14.07
(5.6)
31.92
29.54 (3.4)*
29.33 (3.2)*
129.73
(3.0)
129.75
(3.1)
29.47 (2.0)
29.27 (2.3)
29.19 (2.6)
29.79 (2.6)*
29.60 (2.7)*
29.33 (3.2)
25.02
COOMe
(4.2)
22.68
(2.1)
32.59
(3.1)
130.21
(1.2)
24.71
COOH
14.06
(4.9)
31.91
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29.24 (2.3)
29.31 (2.9)*
29.51 (2.3)
130.22
(3.4)
32.59
(2.1)
29.09 (1.4)
29.18 (1.6)*
29.43 (1.6)
29.59 (1.4)*
29.68 (1.8)*
34.06
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(3.8)
22.21
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32.43
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130.63
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134.17
(1.7)
130.44
(1.2)
29.29
(1.4)
29.08
(2.1)
24.94
COOMe
51.26
(6.6)
13.88
4.5
31.54
2.8
130.75
2.2
133.99
2.0
130.35
1.7
32.71
1.0
28.95
1.2
32.43
1.7
34.07
2.5

Fig. 1.

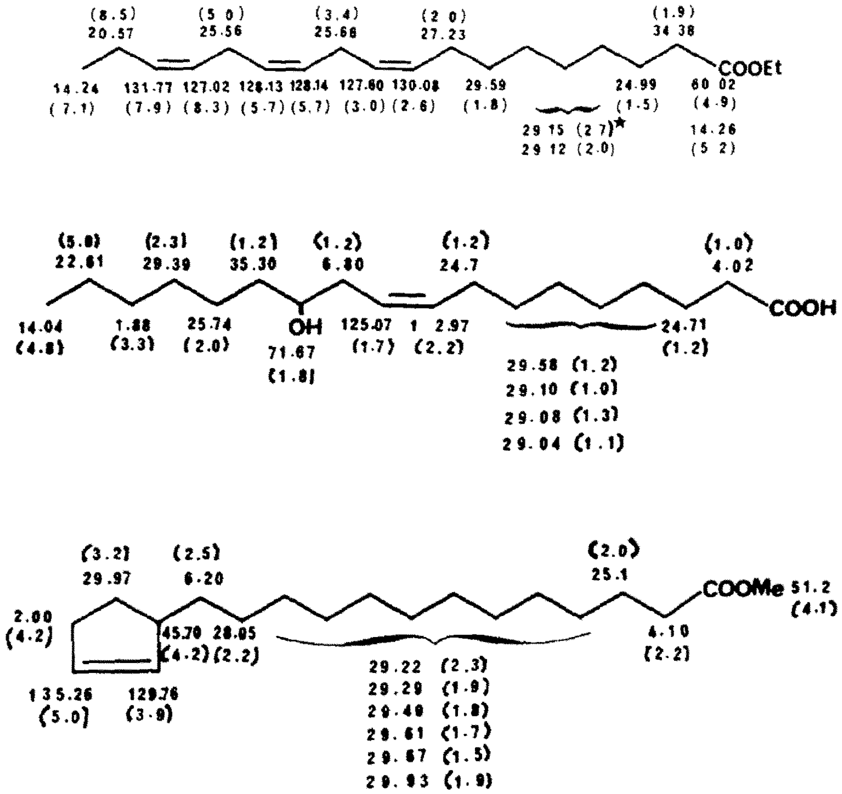

Fig. 1. (Contd)

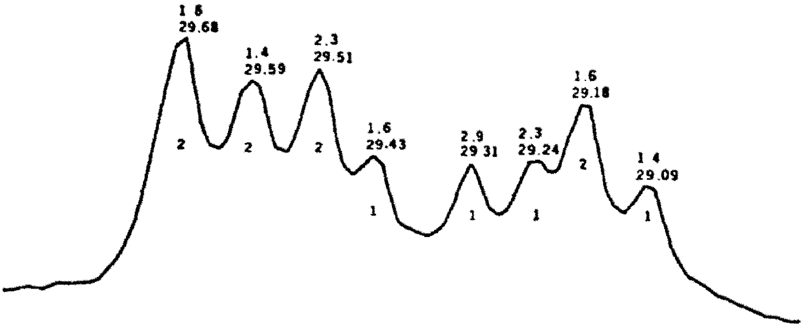

Fig. 2. 29 ppm area of the ^{13}C spectrum of brassidic acid 7. The T_1's (up) and the chemical shifts (down) are shown with each line. The multiplicities are also shown inside each line.

condition by:

$$1/T_1 = (\hbar\gamma_C\gamma_H)^2\tau_c/r^6$$

or:

$$T_1 = Kr^6$$

which gives:

$$T_1{}^d/T_1{}^e = (r_d/r_e)^6 = (1.071/1.091)^6 \neq 0.9.$$

The observed effect must then also be assigned to differences in correlation times: little reorientation must occur around the $-CH-CH_2-$ bonds. The different orientations of the CH and CH_2 fragments can also explain the observed discrepancies. The relaxation of alkenyl carbons was further studied in the two following products: β-elaeostearic acid methyl ester **8** and α-linolenic acid ethyl ester **9**. The three double bonds are closer to the end of the chain in the latter compound and the differences in T_1's appear more clearly. For each double bond the two resonances nearly had the same

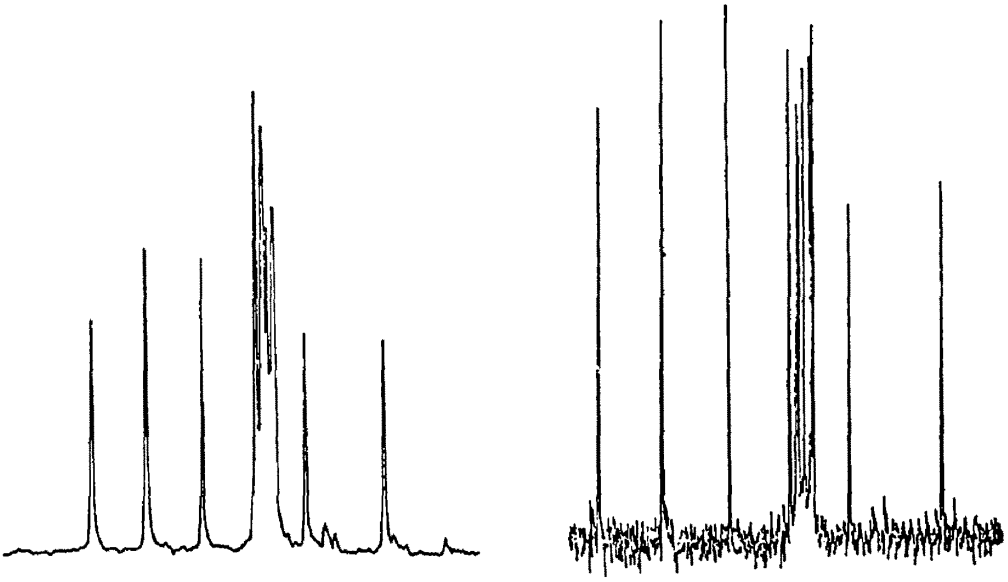

Fig. 3. Expansions (20–40 ppm) of the spectra of chaulmoogric acid methyl ester **11** at 25 MHz (left) and 69 MHz (right).

relaxation time and this time increased towards the end of the chain from one double bond to the other. The same remarks apply (although in a less striking manner) to compound **8**. Although the spectrum of **9** has already been published[7] it should be noted that the T_1's provided a very straightforward assignment of the olefinic resonances. As already mentioned for **1**, the two relaxation times of the carbons forming the double bond are not necessarily in the expected order. This, therefore, cannot be used as an assignment criterion.

The two last compounds (ricinoleic acid **10** and chaulmoogric acid methyl ester **11**) will show the limitations of the method. In these two cases the spectra recorded at 25 MHz were poorly resolved in the 29 ppm area and spectra were recorded again at 69 MHz giving satisfactory results (Fig. 3). The T_1's of **10** increase along the chain in spite of the presence of the hydroxyl function. The spectra of **11** presents 6 peaks near 29 ppm for eight carbon atoms. Nevertheless the relaxation times of these atoms are lower (apart from a slight deviation of 0.1 sec) than those of the two nearest atoms.

CONCLUSION

It has been shown that the segmental motion is responsible for the relaxation behaviour of unsaturated long chain acids and esters. In spite of perturbations in the chain the nT_1's of the acidic compounds increase towards the end of the alkyl chain. In the esters the minimum of the T_1's is located about one third down the length of the complete chain (ester group included) near the carboxyl group. In favorable cases the position of the double bond is determined by the number of atoms having T_1's longer and shorter than those of the carbons adjacent to the double bond. Finally, in the case of multiple double bonds the alkenyl carbon T_1's also increase twoards the end of the chain. This was used as an aid in assigning th ^{13}C spectra of ethyl linolenate **9**.

EXPERIMENTAL

All the compounds were obtained from either Fluka or Roth. 1.5 mmole of each substance was dissolved in 3 ml of $CDCl_3$ containing TMS as an internal standard. Most specrta were recorded on an XL-100 spectrometer operating with disk. The temperature of the probe was regulated to 38°. 32 K data points were used for accumulating the signal. No exponential correction was applied to the FID. The T_1's were obtained by the inversion recovery method. Linear regression on the logarithms of the peak heights yielded T_1's with a typical deviation of 0.03 sec. In two instances the commercially available package was counter-checked by a 3 parameter exponential fit on the head-measured heights. No significant deviations were obtained except for T_1's longer than 5 sec for which the exponential fit gave slightly longer results. As this was not greatly disturbing the results, the commercial program was used routinely. The effect of dissolved oxygen was also checked. Degassing the solution (freeze-pump-thaw) or bubbling nitrogen through it showed little effect except for the longer T_1's. The solutions were used directly.

The reproducibility of the results was also tested by running the same experiment several times. Although the absolute value of the T_1's could undergo changes as large as 1.5 sec from one spectrum to the other, the differences from the T_1 of one carbon to the other (which is the criterion used throughout the text) showed no crossings.

The 69 MHz spectra were recorded at Laboratoire de Biophysique (Ecole Polytechnique) on a home built spectrometer operating with a Bruker magnet. A spectral width of 30 ppm was chosen to allow the maximum number of points (8 K) in the interesting part of the spectra. The decoupler was centered on the aliphatic proton resonances and square wave modulated at 180 Hz. The RF power was limited to 8 W to avoid sample overheating. The temperature was regulated to 38°. The T_1's were obtained by inversion recovery. The heights of the peaks were measured and the results fitted to an exponential curve via a 3 parameter minimization. The T_1 values at 69 MHz were very similar to those obtained at 25 MHz (Typical difference 0.5 sec).

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