Proton Magnetic Resonance Spectra of Unsaturated Fatty Acids

J. M. PURCELL, S. G. MORRIS, and H. SUSI

Eastern Regional Research Laboratory, U. S. Department of Agriculture, 600 East Mermaid Lane, Philadelphia, Pa. 19118

▶ The proton magnetic resonance (PMR) spectra of various unsaturated fatty acids were studied. The types of compounds studied include those in which the methylene chain is interrupted by one or more carbon–carbon multiple bonds. The spectral effects produced by the multiple bonds are discussed. Chemical shifts and, when possible, coupling constants have been determined.

THE PROTON MAGNETIC RESONANCE spectra of many types of organic compounds have been investigated in considerable detail. Various correlation charts, which graphically describe the relation between chemical shift and intramolecular environment, have been published (*1, 9, 10, 14*). Relatively little regarding unsaturated long-chain aliphatic compounds has been reported, although small molecules containing multiple carbon–carbon bonds have been studied extensively. A preliminary investigation of fatty acids and their triglycerides, using high resolution PMR at 40 Mc.p.s., has been reported by Hopkins and Bernstein (*4*). These studies have demonstrated the value of proton magnetic resonance in determining the chemical structure of several types of fatty acids and their derivatives. Johnson and Shoolery investigated the determination of unsaturation in natural fats by PMR (*6*). From this a procedure for calculating an iodine number was devised.

The present communication describes the high resolution 60 Mc.p.s. PMR spectra of a variety of unsaturated fatty acids. Current interest in unsaturated fatty acids indicates the value of additional data on spectra–structure correlations. Compounds in which the methylene chain is interrupted by one or two carbon–carbon multiple bonds are reported. Particular attention is focused on the changes in the PMR spectra produced by *cis-trans* isomerism and by conjugation. The highly complex spin systems formed by these molecules often give rise to broad unresolved or partially resolved multiplets, which result from a large number of closely spaced transitions. It is, therefore, not always possible to measure corresponding spin coupling constants. The broad multiplets are nevertheless useful as fingerprint patterns and permit one to distinguish among similar structural groupings involving multiple carbon–carbon bonds.

EXPERIMENTAL

The spectra of all samples were obtained at ambient temperature—i.e., 33° ± 1° C.—in the magnet air gap with a Varian DP-60 nuclear magnetic resonance spectrometer. The amplitude of the radio field was set at 60 db. down from one-half watt so as to avoid saturation of signals. The external magnetic field was swept at the rate of 0.5 to 1.0 c.p.s./second. Spectral resolution was 0.6 c.p.s. or better. Calibration of the spectra was accomplished by the usual side-band technique, using a Hewlett-Packard 200 CD wide-band oscillator and a 522B electronic counter. Line position measurements were accomplished with the aid of an instrument developed in this laboratory (*11*). Tetramethylsilane (K & K Laboratories Inc., Jamaica, N. Y.) was used as an internal reference.

Each spectrum was recorded 10 times to reduce the possibility of instrumental error. Chemical shift values are based on the averages of the measured line positions. The *delta* scale is used to report chemical shifts, where $\delta = 0.00$ for tetramethylsilane with positive values to low field. Certain complex multiplets were located by stating the position of the midpoint. Olefinic protons in *trans*-octadec-11-en-9-ynoic acid, 2-*cis*-octadecenoic acid, and 2-*trans*-octadecenoic acid give rise to an AB quartet. Therefore, the coupling constant can be measured directly, whereas the chemical shifts must be computed from the coupling constants and the separation between the A and B resonances (*13*). The separation between the centers of the A and B doublets in equal to $[J^2 + (\nu_A - \nu_B)^2]^{1/2}$. The computed chemical shift value in c.p.s. is the chemical shift of the A and B protons relative to each other. For comparison this single value must be converted to a δ value for each proton. The midpoint of the AB quartet corresponds to a certain positive value in terms of c.p.s. downfield from tetramethylsilane. One-half of the computed chemical shift is added to and subtracted from this latter value to obtain the chemical shifts in c.p.s. from tetramethylsilane of the A and the B protons.

Pure crystalline or liquid samples dissolved in carbon tetrachloride (Spectroquality Reagent, Matheson, Coleman and Bell, East Rutherford, N. J.) or deuterochloroform (Varian Associates, Palo Alto, Calif.) were used. The concentration range of the solutions was 0.1 to 0.4*M*.

Polyunsaturated fatty acids were prepared as follows:

10,12-Octadecadiynoic acid was obtained from 1-bromopentane and 10-undecenoic acid. 1-Bromopentane was reacted with sodium acetylide in liquid ammonia to form 6-heptyne (*5*). 10-Undecenoic acid was brominated and then dehydrobrominated to form 10-undecynoic acid. The two acetylenic compounds were oxidatively coupled to form 10,12-octadecadiynoic acid, m.p. 44.3°–45° C.

10,12-*cis,cis*-Octadecadienoic acid was obtained through hydrogenation of 10,12-octadecadiynoic acid with a Lindlar catalyst (*8*).

9,11-*trans,trans*-Octadecadienoic acid, m.p. 53.3–53.6° C., was prepared from methyl 12-chlorooleate, obtained by treating methyl ricinoleate with thionyl chloride (*2*). Methyl 12-chlorooleate was refluxed in alcoholic KOH (500 ml. of ethanol, 25 grams of KOH in 25 ml. of water) for 10 hours. On acidification the acid was taken up in ether, washed, dried, and crystallized three times from petroleum ether.

trans-Octadec-11-en-9-ynoic acid (santalbic acid), m.p. 38.5–39.5° C., was obtained from santalum album seed oil by the procedure of Gunstone and Russell (*3*).

Methyl 9,12-octadecadienoate (methyl linoleate) was prepared from methyl esters of safflower oil by a series of urea complex precipitations, followed by fractional distillation. The product was analyzed by GLC and proved to be 99+% pure.

9,12-*trans,trans*-Octadecadienoic acid (linoelaidic acid), m.p. 28° C., was obtained from methyl linoleate by the procedure of Kass and Burr (*7*), followed by saponification. The product was crystallized twice from methanol containing a small amount of water at 22° C., followed by two crystallizations from light petroleum.

9-*cis*-Octadecenoic acid (oleic acid), m.p. 14.0–14.5° C., 9-*trans*-octadecenoic acid (elaidic acid), m.p. 38.5–39.5° C., 2-*cis*-octadecenoic acid, m.p. 50.5–51.0° C., and 2-*trans*-octadecenoic acid, m.p. 58.0–58.5° C., were obtained by standard procedures.

Table I. Identification of the Chemical Shifts and the Spin-Spin Splittings of Various Protons

Compound	Spectrum no.	Proton	Chemical shifts	No. of observed lines
$\overset{a}{CH_3}(\overset{b}{CH_2})_6\overset{c}{CH_2}\overset{e}{CH}{=}\overset{e}{CH}\overset{c}{CH_2}(\overset{b}{CH_2})_5\overset{d}{CH_2}C({=}O)OH$	1A	a	0.89	3
		b	1.27	1
9-*cis*-octadecenoic acid		c	1.98	2
		d	2.30	3
		e	5.27	3
$\overset{a}{CH_3}(\overset{b}{CH_2})_6\overset{c}{CH_2}\overset{e}{CH}{=}\overset{e}{CH}\overset{c}{CH_2}(\overset{b}{CH_2})_5\overset{d}{CH_2}C({=}O)OH$	1B	a	0.88	3
		b	1.27	1
9-*trans*-octadecenoic acid		c	1.90	1
		d	2.29	3
		e	5.31	3
$\overset{a}{CH_3}(\overset{b}{CH_2})_4\overset{c}{CH_2}\overset{e}{CH}{=}\overset{e}{CH}{-}\overset{e}{CH}{=}\overset{e}{CH}\overset{c}{CH_2}(\overset{b}{CH_2})_5\overset{d}{CH_2}C({=}O)OH$	2A	a	0.87	3
		b	1.31	1
9,11-*trans,trans*-octadecadienoic acid		c	2.03	3
		d	2.33	2
		e	5.9[a]	10
$\overset{a}{CH_3}(\overset{b}{CH_2})_3\overset{c}{CH_2}\overset{e}{CH}{=}\overset{e}{CH}{-}\overset{e}{CH}{=}\overset{e}{CH}\overset{c}{CH_2}(\overset{b}{CH_2})_6\overset{d}{CH_2}C({=}O)OH$	2B	a	0.89	3
		b	1.30	1
10,12-*cis,cis*-octadecadienoic acid		c	2.03	3
		d	2.29	2
		e	5.7[a]	10
$\overset{a}{CH_3}(\overset{b}{CH_2})_3\overset{c}{CH_2}C{\equiv}C{-}C{\equiv}C{-}\overset{c}{CH_2}(\overset{b}{CH_2})_6\overset{d}{CH_2}C({=}O)OH$	3A	a	0.92	3
		b	1.38	1
10,12-octádecadiynoic acid		c	2.19	2
		d	2.33	2
$\overset{a}{CH_3}(\overset{b}{CH_2})_4\overset{c}{CH_2}\overset{g}{CH}{=}\overset{f}{CH}{-}C{\equiv}C\overset{d}{CH_2}(\overset{b}{CH_5})_2\overset{e}{CH}C({=}O)OH$	3B	a	0.91	3
Trans-octadec-11-en-9-ynoic acid		b	1.3[a]	3
		c	2.11	2
		d	2.26	2
		e	2.36	2
		f	5.43	2
		g	6.00	6
$\overset{a}{CH_3}(\overset{b}{CH_2})_3\overset{c}{CH_2}\overset{f}{CH}{=}\overset{f}{CH}\overset{e}{CH_2}\overset{f}{CH}{=}\overset{f}{CH}\overset{c}{CH_2}(\overset{b}{CH_2})_5\overset{d}{CH_2}C({=}O)OCH_3$	4A	a	0.88	3
		b	1.31	1
Methyl 9,12-*cis,cis*-octadecadienoate		c	2.03	3
		d	2.22	3
		e	2.72	3
		f	5.27	15
$\overset{a}{CH_3}(\overset{b}{CH_2})_3\overset{c}{CH_2}\overset{f}{CH}{=}\overset{f}{CH}\overset{e}{CH_2}\overset{f}{CH}{=}\overset{f}{CH}\overset{c}{CH_2}(\overset{b}{CH_2})_5\overset{d}{CH_2}C({=}O)OH$	4B	a	0.90	3
		b	1.32	1
9,12-*trans,trans*-octadecadienoic acid		c	1.94	1
		d	2.30	3
		e	2.61	1
		f	5.32	3
$\overset{a}{CH_3}(\overset{b}{CH_2})_{13}\overset{c}{CH_2}\overset{e}{CH}{=}\overset{d}{CH}C({=}O)OH$	5A	a	0.89	3
		b	1.26	1
2-*cis*-octadecenoic acid		c	2.66	2
		d	5.75	2
		e	6.29	6
$\overset{a}{CH_3}(\overset{b}{CH_2})_{13}\overset{c}{CH_2}\overset{e}{CH}{=}\overset{d}{CH}C({=}O)OH$	5B	a	0.90	3
		b	1.27	1
2-*trans*-octadecenoic acid		c	2.21	2
		d	5.76	2
		e	7.02	6

[a] This value is not a chemical shift but serves merely to locate approximately a complex multiplet.

RESULTS AND DISCUSSION

The structural formulas of the investigated compounds, the observed chemical shifts and the number of observed lines are listed in Table I. The acid proton was not considered. The PMR spectra of saturated long-chain carboxylic acids, which could be regarded as the parent compounds of the investigated unsaturated derivatives, exhibit three main peaks (*4*, *12*). A high-field triplet at $\delta = 0.87$ to 0.92 corresponds to the terminal methyl group. The chain methylene groups produce a broad band at $\delta = 1.25$ to 1.35. A low-field triplet is produced by the alpha methylene group, adjacent to the carboxyl group, and falls in the range $\delta = 2.25$ to 2.35. In most fatty acid spectra the triplet of the terminal methyl group is somewhat broadened and distorted. Only two lines of the alpha methylene triplet are clearly discernible. The third or low-field line of this triplet always appears as a kind of "shoulder" to the center band.

Isolated Double Bonds. The introduction of multiple carbon-carbon bonds into the methylene chain of a long-chain molecule has a deshielding effect upon the olefinic protons and upon the first methylene group on either side of the multiple bond. The PMR spectra of 9-*cis*-octadecenoic acid (oleic acid) (Figure 1*A*) and 9-*trans*-octadecenoic acid (elaidic acid) (Figure 1*B*) exhibit "doublets" at $\delta = 1.98$ and $\delta = 1.90$, respectively, representing the methylene groups adjacent to the double bond. The downfield shift from the chain methylene position is approximately 0.7 p.p.m. These apparent doublets overlap both the broad band of the chain methylene groups and the alpha methylene triplet. In the oleic acid spectrum the apparent doublet is only partially resolved; in the elaidic acid spectrum no line separa-

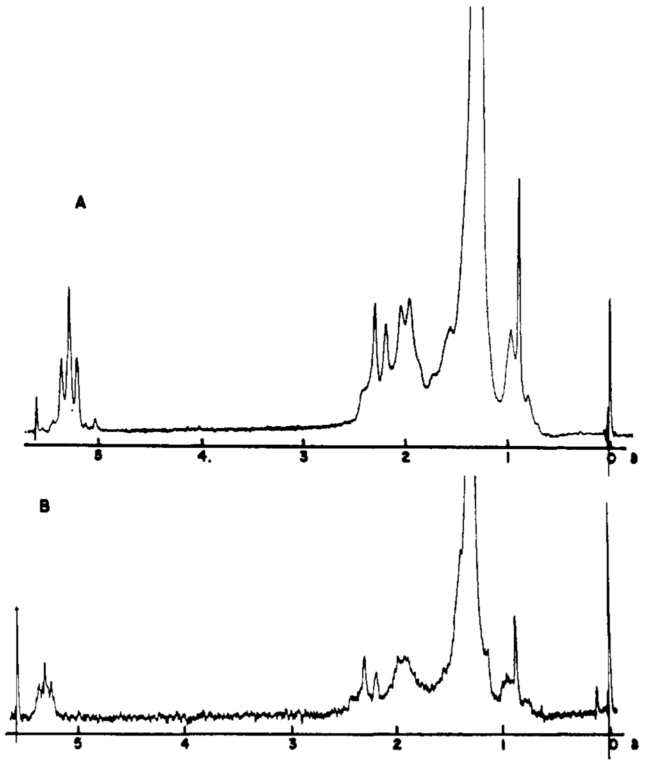

Figure 1. PMR spectra of fatty acids with one isolated double bond

A. 9-*cis*-octadecenoic acid
B. 9-*trans*-octadecenoic acid

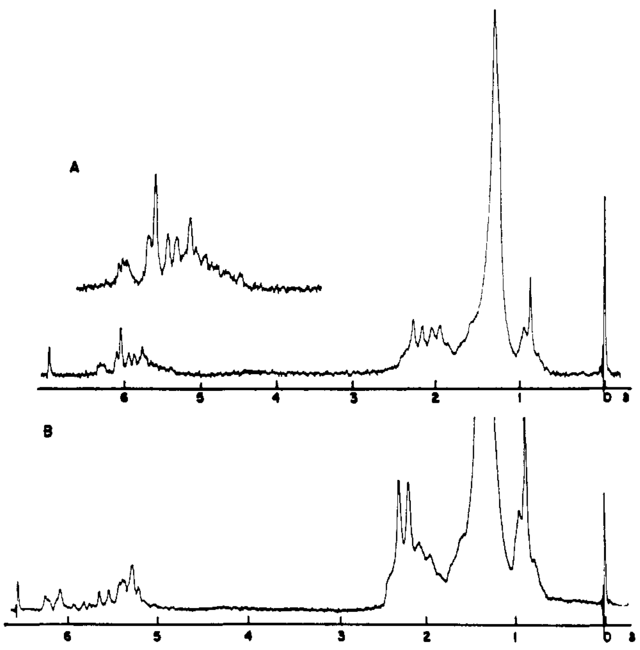

Figure 2. PMR spectra of fatty acids with conjugated double bonds

A. 9,11-*trans,trans*-octadecadienoic acid
B. 10,12-*cis,cis*-octadecadienoic acid

tion is observed. The broad lines are actually envelopes of a large number of closely spaced transitions. It is, therefore, not possible to evaluate coupling constants from the experimental data. Nevertheless the broad lines are sufficiently different in appearance to be useful as fingerprint patterns.

The olefinic protons of oleic and elaidic acids give rise to multiplet patterns at $\delta = 5.27$ and 5.31, respectively. The pattern representing the *cis* configuration appears to be a triplet, though partially obscured by line broadening (Figure 1*A*). The *trans* configuration is indicated by a broad band almost completely devoid of detail (Figure 1*B*).

Two Conjugated Multiple Bonds. Conjugated multiple bonds occur in 9,11-*trans, trans*-octadecadienoic acid (Figure 2*A*), in 10,12 - *cis,cis*-octadecadienoic acid (Figure 2*B*), in 10,12-octadecadiynoic acid (Figure 3*A*) and in trans-octadec-11-en-9-ynoic acid (santalbic acid) (Figure 3*B*). Methylene groups adjacent to the conjugated system appear as broadened quartets at $\delta = 2.03$ in both the *trans,trans* and *cis,cis* dienoic acids. The two center lines are observable in both cases; the high-field line is just barely discernible; the low-field line overlaps the alpha methylene triplet ($\delta = 2.30$). A priori, it is difficult to predict the proton spin coupling pattern. The quartet pattern probably results from coupling between the methylene group adjacent to the double bond and the three protons, one olefinic and two methylene, adjacent to it. On this basis, the quartet might be classified as the A_2 portion of an A_2X_3 spin system, except that this spin system is but a part of a much more complex system giving rise to a large number of transitions.

The methylene groups adjacent to the conjugated triple bonds in 10,12-octadecadiynoic acid appear as a broadened triplet at $\delta = 2.19$ (Figure 3A). This triplet apparently overlaps the alpha methylene triplet, which usually occurs at about $\delta = 2.30$. The low-field of the observed triplet is taken as the center band of the alpha methylene triplet ($\delta = 2.33$). Line broadening has the same cause and consequence as is mentioned above.

trans - Octadec - 11 - en - 9 - ynoic acid (Figure 3*B*) containing a double and a triple bond in a conjugated sequence, presents a composite of the above situations. On the basis of the foregoing information one would predict the overlapping of a broadened triplet

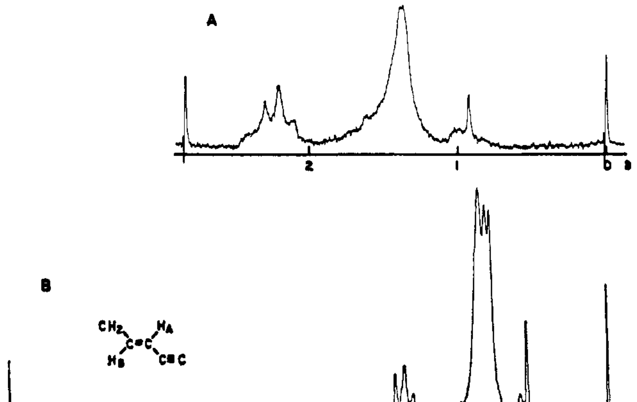

Figure 3. PMR spectra of fatty acids with conjugated multiple bonds

A. 10,12-octadecadiynoic acid
B. *Trans*-octadec-11-en-9-ynoic acid

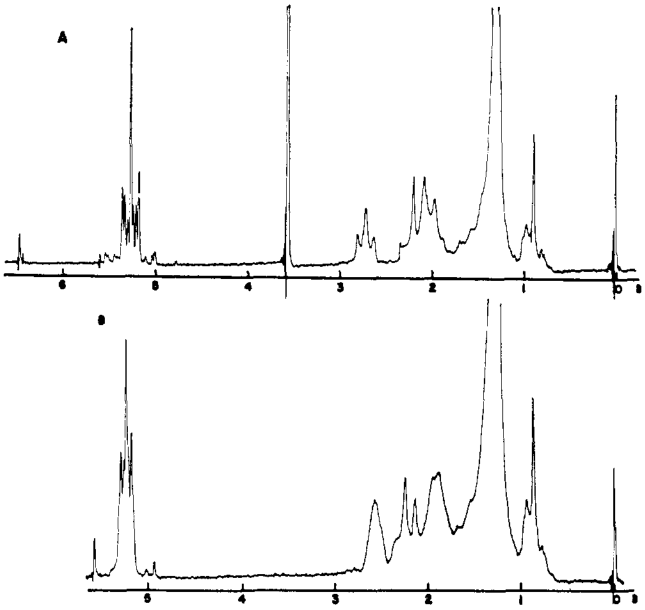

Figure 4. PMR spectra of fatty acids with two double bonds separated by one methylene group

A. methyl 9,12-*cis,cis*-octadecadienoate
B. 9,12-*trans,trans*-octadecadienoic acid

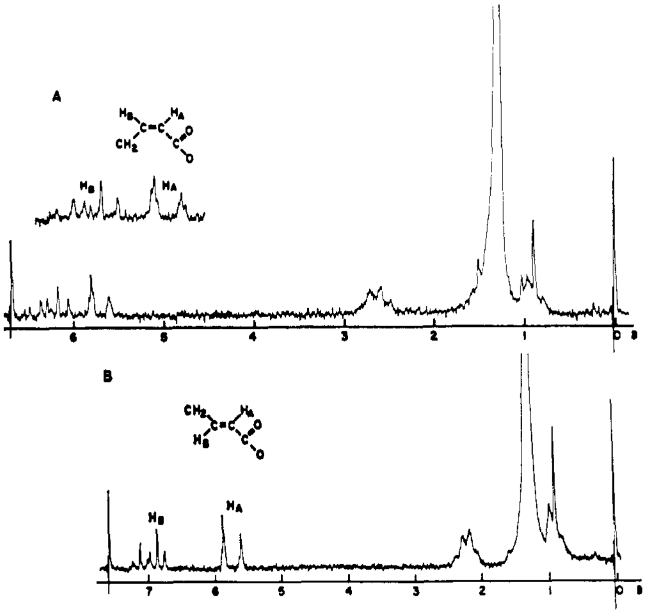

Figure 5. PMR spectra of fatty acids with a double bond adjacent to a carboxyl group

A. 2-*cis*-octadecenoic acid
B. 2-*trans*-octadecenoic acid

representing the methylene group adjacent to the triple bond, and a broadened quartet, representing the methylene adjacent to the double bond, complicated by the overlapping with the alpha methylene triplet. The observed spectrum between $\delta = 2.0$ and 2.5 probably fits this description, although the three multiplets are discernible only with some difficulty, because overlapping obscures portions of each of them. Chemical shift assignments are as follows: the methylene group adjacent to the double bond at $\delta = 2.11$, the methylene group adjacent to the triple bond at $\delta = 2.26$, and the alpha methylene group at $\delta = 2.36$. It is noted that each of these positions is slightly downfield from the similar chemical shifts stated above. It should also be mentioned that the chain methylene groups in this molecule produce three observable lines, one of which is very broad, instead of a single broad band. No attempt to analyze this pattern has been made; however, the three line positions correspond to δ values of 1.30, 1.35, and 1.42.

The olefinic protons of 9,11-*trans, trans*- and 10,12-*cis,cis*-octadecadienoic acids exhibit complex spin coupling patterns centered at approximately $\delta = 5.9$ and $\delta = 5.7$, respectively (Figures 2*A* and 2*B*). No attempt to analyze these patterns has been made. From the figures it is seen that the two patterns are significantly different and would be useful as fingerprint patterns. The spectrum of *trans*-octadec-11-en-9-ynoic acid (Figure 3*B*) displays an olefinic proton multiplet quite similar to that displayed in the spectrum of 2-*cis*-octadecenoic acid (*infra*). The entire multiplet consists of eight observable lines. An AB quartet is produced by the olefinic protons. The low-field doublet is further split into two triplets due to the coupling of one olefinic proton with the adjacent methylene group. The coupling constants and the calculated chemical shifts are as follows: $J_{CH_2-H_B} = 6.57$ c.p.s., $J_{AB} = 16.31$ c.p.s., $\delta_A = 5.43$, $\delta_B = 6.00$ (H_A and H_B are defined in Figure 3*B*).

Double Bonds Separated by One Methylene Group. Nonconjugated carbon - carbon double bonds, separated by one methylene group, occur in methyl 9,12-*cis,cis*-octadecadienoate (methyl linoleate) (Figure 4*A*) and in 9,12-*trans,trans*-octadecadienoic acid (Figure 4*B*). Methylene groups adjacent to the double bonds in the *cis,cis* compound exhibit a broadened, partially-resolved quartet at $\delta = 2.03$. The low-field line overlaps the alpha methylene triplet at $\delta = 2.22$, whereas the corresponding groups in the *trans,trans* acid produce only a broad band devoid of detail at $\delta = 1.94$. Negligible overlapping with the alpha methylene triplet at $\delta = 2.30$ occurs in the latter case. The methylene group between the two double bonds appears in the spectrum of the *cis,cis* compound as a partially resolved triplet at $\delta = 2.72$. Only a single broad band at $\delta = 2.61$ is displayed by the corresponding group in the spectrum of the *trans,trans* acid. With respect to both types of methylene groups, the chemical shift in the *cis,cis* compound is 0.1 p.p.m. greater than in the *trans,trans* acid.

A sharp contrast between the olefinic proton multiplets is observed (Figures 4*A* and 4*B*). The *cis* olefinic protons display a complex multiplet at $\delta = 5.27$ in which 15 sharp lines are observed (Figure 4*A*), whereas the *trans* olefinic protons display a partially-resolved "triplet" at $\delta = 5.32$.

Double Bonds Adjacent to the Carboxyl Group. A carbon-carbon double bond in juxtaposition to a carboxyl group is present in 2-*cis*-octadecenoic acid (Figure 5*A*) and in 2-*trans*-octadecenoic acid (Figure 5*B*). In both compounds the alpha methylene group is absent, and the methylene groups adjacent to the double bonds occur at $\delta = 2.66$ and $\delta = 2.21$, respectively. Both appear as very broad bands almost devoid of detail. The olefinic protons in both compounds exhibit an AB quartet with the low-field doublet further split into two triplets. The triplet pattern arises from the spin coupling of one olefinic proton with the adjacent methylene group. The entire olefinic proton multiplet consists of eight lines. A similar pattern is produced by the olefinic protons of *trans*-octadec-11-en-9-ynoic acid mentioned above. The coupling constants and the calculated chemical shifts are as follows: 2-*cis*- $J_{CH_2-H_B} = 5.78$ c.p.s., $J_{AB} = 11.31$ c.p.s., $\delta_A = 5.75$, $\delta_B = 6.29$; 2-*trans*- $J_{CH_2-H_B} = 6.67$ c.p.s., $J_{AB} = 15.51$ c.p.s. $\delta_A = 5.76$, $\delta_B = 7.02$. (H_A and H_B are defined in Figure 5.)

LITERATURE CITED

(1) Chamberlain, N. F., Anal. Chem. 31, 56 (1959).
(2) Grigor, J., MacInnes, D. M., McLean, J., Hogg, A. J. P., *J. Chem. Soc.* **1955**, 1069.

(3) Gunstone, F. D., Russell, W. C., *Ibid.*, 3782.
(4) Hopkins, C. Y., Bernstein, H. J., *Can. J. Chem.* **37**, 775 (1959).
(5) Jacobs, T. L., "Organic Reactions," Vol. **5**, p. 48, Wiley, New York, 1949.
(6) Johnson, L. F., Shoolery, J. N., Anal. Chem. **34**, 1136 (1962).
(7) Kass, J. P., Burr, G. O., *J. Am. Chem. Soc.* **61**, 1062 (1939).
(8) Lindlar, H., *Helv. Chim. Acta* **35**, 446 (1952).
(9) Meyer, L. H., Saika, A., Gutowsky, H. S., *J. Am. Chem. Soc.* **75**, 4567 (1953).
(10) Nukada, K., Yamamota, O., Suzuki, T., Takeuchi, M., Ohnishi, M., Anal. Chem. **35**, 1892 (1963).
(11) Purcell, J. M., Connelly, J. A., *Ibid.*, **37**, 1181 (1965).
(12) Purcell, J. M., Susi, H., *Appl. Spectr.* **19**, 105 (1965).
(13) Roberts, J. D., "An Introduction to the Analysis of Spin-Spin Splitting in Nuclear Magnetic Resonance Spectra," p. 57, W. A. Benjamin Inc., New York, 1961.
(14) Tiers, G. V. D., "Characteristic Nuclear Magnetic Resonance Shielding Values for Hydrogen in Organic Structures," Part I: Tables of τ-Values for a Variety of Organic Compounds, Minnesota Mining and Manufacturing Co., St. Paul, Minn., 1958.

Received for review September 28, 1965. Accepted February 2, 1966. First Middle Atlantic Regional Meeting, ACS, Philadelphia, Pa., February 3–4, 1966. Mention of commercial products does not constitute an endorsement by the United States Department of Agriculture over others of a similar nature not mentioned.

Relationship Between Resonance Line Profile and Absorbance in Atomic Absorption Spectrometry

KAZUO YASUDA

Application Laboratory, Naka Works, Hatachi Ltd., Katsuta-shi, Ibaraki-ken, Japan

▶ The relationship between the profile of the resonance emission line of the calcium hollow cathode lamp and the absorbance of calcium atomic vapor in the flame, and the relationship between the profile of the resonance absorption line of calcium in the flame and its absorbance were studied theoretically. It was found that the decrease in the absorbance of calcium in the flame caused by the increase in the discharge current of the lamp is due to the self-absorption of the resonance emission line from the lamp, and that the increase in the Döppler breadth of the resonance emission line has a slight effect on the absorption intensity. The center of the resonance absorption line of the flame shifts to longer wavelength, and the resonance absorption line is not symmetrical. Consequently, the difference in the relationship between the absorbance of the flame and the discharge current in various flames is presumably due to the shift and asymmetry of the absorption line.

In atomic absorption spectrometry, the profiles of the resonance emission line and the resonance absorption line have an influence on the absorbance of atomic vapor in the flame (*7*). In order to increase the absorbance (*1, 4*), the atomic vapor temperature, gas pressure, and the degree of self-absorption, all of which determine the breadth of the resonance emission line from a hollow cathode lamp as a light source, must be low values.

In developing the initial theory of atomic absorption spectrometry, Walsh (*9*) assumed that the breadth of the resonance emission line from a hollow cathode lamp is extremely narrow, that the central wavelength of the resonance emission line from the lamp corresponds to the central wavelength of the resonance absorption line, and that the breadth of this absorption line is determined by the Döppler effect.

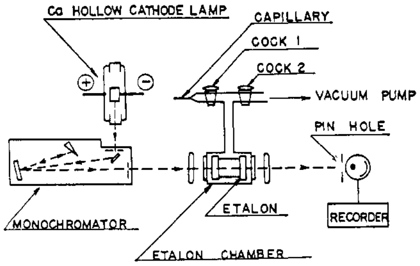

Figure 1. Schematic diagram of pressure-scanning Fabry–Perot interferometer

Shimazu and Hashimoto (*8*) measured sodium line profiles, and showed that the breadth of the resonance emission line from the sodium discharge lamp is of the same order as the resonance absorption line breadth of sodium in the air–acetylene flame, and that an increase in the self-absorbance of the resonance emission line caused a decrease in the absorbance of the flame.

Winefordner (*10*) made clear theoretically that the absorbance is independent of the absorption line breadth as long as the breadth of the resonance emission line from the lamp is much smaller than the breadth of the resonance absorption line.

The relatively high density of gases in flames at atmospheric pressure results in a resonance absorption line with extensive collisional broadening. The relationship between the discharge current of the calcium hollow cathode lamp and the absorbance of calcium in a flame is different according to the kind of flame—i.e., oxyhydrogen, oxypropane, or oxyacetylene. This may be due to the fact that there is a shift in the absorption line (*3*).

We studied the following two subjects: (1) the determination of the profile of the resonance emission line from the calcium hollow cathode lamp, and the relationship between the increase in the Döppler breadth or the degree of self absorption of the resonance emission line and the absorbance of calcium in the flame; and (2) the determination of the resonance absorption line profile of calcium in the flame, and the difference in the absorbance of calcium in various flames.

EXPERIMENTAL

Measurement of the Profile of the Resonance Emission Line from the Calcium Hollow Cathode Lamp. The breadth of the resonance emission line from the lamp is related to the temperature of calcium atomic vapor. The temperature of atomic vapor in the discharge is higher than the cathode temperature. By the use of the pressure scanning Fabry–Perot interferometer, shown in Figure 1, the profile of the resonance emission line at various discharge currents was observed.

The emission lines from the lamp (the hollow cathode was made of calcium aluminum alloy) were dispersed by the monochromator, and the bright lines 4228.9, 4227.5, and 4226.8 A. of aluminum neighboring the calcium resonance line at 4226.7 A. were excluded. Only one resonance emission line was introduced into the interferometer. After the etalon chamber was evacuated, air was introduced gradually into the chamber by opening stopcock 1 (see Figure 1). The interference fringe at the center grew with the increase of air pressure in the chamber. The intensity at the center of the fringe was determined with the photomultiplier tube.