^{13}C NMR Spectroscopy of Unsaturated Long-chain Compounds: an Evaluation of the Unsaturated Carbon Signals as Rational Functions

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Literature data on the ^{13}C NMR spectra of unsubstituted monounsaturated fatty acids and esters as well as fatty acids and esters with allylic hydroxy groups between the double bond and the terminal methyl group have been evaluated. The signals of the unsaturated carbons between the functional group at C-1 and the position of shift equivalence (POSE; defined as the location of the double bond where the separations of the olefinic carbon signals becomes zero in unsubstituted compounds) are of special interest because they depend on the distance of the unsaturation from C-1. The resonances of both unsaturated carbons as well as their difference (the shift value of the carbon closer to C-1 is subtracted from that of the C closer to the terminal methyl group) are rational functions. The equations for the *s* are the difference of the equations for the individual unsaturated carbons. When comparing *Z* and *E* unsaturation, the equations for *s* do not differ but those for the individual olefinic carbons differ. Some octadecadienoic acids are also discussed. The results generally agree with the electric field model presented by other authors for explaining the decreases in shift separations.

The ^{13}C NMR spectra of various fatty compounds have been recorded and discussed extensively.[1] In the case of alkenes and unsaturated fatty compounds, additive or subtractive increments for the signals of selected carbons were determined relative to standards to predict the position of the double bond.[1-4] In the spectra of unsaturated fatty compounds, the separation of the signals of the unsaturated carbons decreases with increasing distance of the double bond from the functional group at C-1.[1,5-10]

Some examples (octadecenoic, octadecynoic and some octadecadienoic acids) from earlier literature[5,6] as well as allylic hydroxy fatty compounds[9,10] were selected for evaluation. In a previous paper,[9] we mentioned that the separation of the ^{13}C NMR signals of the olefinic carbons in allylic hydroxy fatty acids with the hydroxy group located on the methyl terminus side (referred to in the following text as position II compounds; the corresponding substances with the hydroxy group on the functional group side are termed position I compounds) could presumably be evaluated as a rational function. Here we report that the evaluation indeed yields rational functions for the shifts of unsubstituted and position II hydroxy olefinic fatty compounds inversely related to the third power of the double bond distance from C-1. In the case of unsubstituted acetylenic fatty acids, the signals of the unsaturated carbons are inversely related to the second power of their distance from C-1. The results hold for all unsaturated positions between the functional group at C-1 and the POSE (= position of shift equivalence; defined as the location of the double bond where the resonance differences of the carbons become 0, *i.e.* the two signals of the olefinic carbons degenerate into one signal in unsubstituted compounds).

Results and Discussion

Several data series in the literature were suitable for evaluation. Criteria for selection were: (*i*) a chain long enough to have the signals of both unsaturated carbons degenerate into one resonance at some distance from the functional group at C-1 (the POSE; usually located at C-12 for C-18 chain length for unsubstituted compounds) and (*ii*) data for isomers with the unsaturation at numerous positions in the chain.

The selections comprise octadecenoic acids with unsaturations from C-3 to -17,[5] octadecynoic acids with triple bonds from C-2 to C-17,[6] and some octadecadienoic acids.[5,8] Besides these compounds, we evaluated allylic hydroxy fatty compounds.[9,10] Only position II hydroxy fatty compounds were evaluated because lactonization occurs for position I compounds up to C-6[9,10] and in position I compounds the hydroxy group largely blocks the effect of the functional group at C-1.[9]

Definitions.—The term 'unsubstituted compounds' as used in this paper will refer to unsaturated compounds containing only a functional group (carboxy or methyl ester) at C-1.

For the subsequent discussion, the following symbols are defined: *s* denotes the separation of the unsaturated carbon signals in ppm ($s = 0$ at the POSE for unsubstituted compounds; note that *s* is often represented by $\Delta\delta$ in case of double bonds in other literature), *u* represents the position of the unsaturation (for example a double or triple bond at C-3–C-4 will receive, analogous to nomenclature, the value $u = 3$), *a* is a factor as determined below, *b* is the power of *u*, and *f* is an additive or subtractive correction factor. The term *z* is a base value for calculating the shifts of the individual unsaturated carbons. The signal of the unsaturated carbon closer to the functional group at C-1 is resonance 1 (similar to position I of the allylic hydroxy fatty compounds; abbreviated R_1 in any equation). The signal of the unsaturated carbon closer to the terminal methyl group is resonance 2 (similar to position II; abbreviated R_2 in any equation). The subscript *x* in some equations refers to the subscripts 1 or 2 of the olefinic carbons. Because the resonance values for R_2 are larger than those of R_1 for locations of the double bond between C-1 and the POSE, the difference [eqn. (1)] gives *s* a positive sign. For locations

$$s = R_2 - R_1 \qquad (1)$$

beyond the POSE, *s* becomes negative as examination of literature data[1] reveals.

Determining the Equations.—To our knowledge, this is the first report on ^{13}C NMR spectroscopy of fatty compounds with the exception of ref. 10 where the actual values or separations of the signals are plotted against *u*, although figures approaching such plots appeared for homoallylic and bis-homoallylic

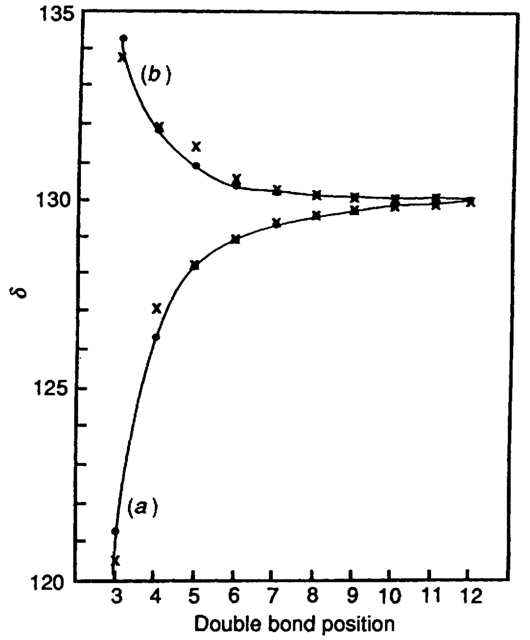

Fig. 1 Plots of the ^{13}C NMR signals of the olefinic carbons in unsubstituted octadecenoic acids using data supplied by Gunstone *et al.*[5] The difference between these plots gives rise to the shift separation plotted in Fig. 2. The plots depict the functions [eqns. (4) and (5)] which approximate the datapoints while the datapoints for the measured values are also shown.

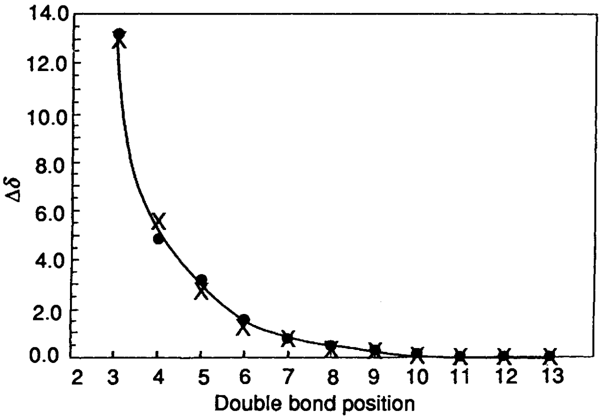

Fig. 2 Plot of the separation of the ^{13}C NMR olefinic carbon signals (see Fig. 1) in unsubstituted octadecenoic acids *vs.* the double bond position (the datapoints are located on the olefinic carbon closest to the functional group at C-1, which also corresponds to nomenclature). The plot depicts eqn. (6), which approximates the datapoints.

hydroxy fatty esters[11] and unsaturated fatty acids.[3,12] Plots of the olefinic resonances of (Z)-octadecenoic acids *vs.* u (see Fig. 1) using data provided by Gunstone *et al.*[5] and of s *vs.* u (Fig. 2) revealed that there must exist mathematical functions for describing the dependence of R_1, R_2 and s on u. These functions are valid only for the unsaturated positions between the functional group at C-1 (and only for the positions for which data are available) and the POSE. The functions were determined semiempirically by testing various equations for the quality of their approximation.

We found that rational functions with the general eqn. (2)

$$R_x = z_x \pm (a_x/u^b) \qquad (2)$$

give the best approximation for the shifts of the individual unsaturated carbons.

Table 1 Observed and calculated separations (ppm) of the olefinic carbon shifts in unsubstituted (Z)- and (E)-octadecenoic acids[a]

	Z		E
Double bond position	$s_{\text{obsd.}}$	$s_{\text{calcd.}}$	$s_{\text{obsd.}}$
3	13.21	13.13	—
4	4.90	5.42	—
5	3.23	2.68	3.26
6	1.61	1.47	1.64
7	0.86	0.85	0.92
8	0.52	0.50	0.54
9	0.31	0.29	0.31
10	0.17	0.16	0.16
11	0.07	0.07	0.08
12	0.00	0.01	0.00

[a] The observed separations were calculated from data in ref. 5 (for actual shift values as basis of the calculated separations and Fig. 1, see ref. 5). The calculated data are approximated by eqn. (6). For a plot see Fig. 2.

Rational functions with the general formula (3) give the best

$$s = (a/u^b) \pm f \qquad (3)$$

approximation of the plots of s *vs.* u for s defined according to eqn. (1).

The factor a in eqn. (3) was determined by multiplying u^b for different b with s of the unsaturation closest to C-1 as determined from the literature data. It was then rounded to one of the nearest factors of 10. The factor f, which also depends on the nature of the functional group at C-1, is necessary for the rational functions to obtain the value $s = 0$ at the POSE for unsubstituted compounds. f is the value of the term (a/u^b) at the POSE. Thus both a and f were determined semiempirically in similar fashions from the data and the procedure guaranteed that both 'ends' of the function (*i.e.*, greater and smaller u) were accounted for in the resulting equations.

A similar procedure can be used to determine the equations for R_1 and R_2. Note that $z_2 - z_1 = f$. The z values used for calculating the shifts of the individual unsaturated carbons are not identical to the shift value of the POSE and were determined empirically. The parameters f and z improve the correlation of the rational functions to the measured values at double bond locations between C-1 and the POSE. Both factors depend on the functional group at C-1. In the case of z, this dependence is displayed by its deviation from the shift value of the POSE.

The same evaluation procedure was applied to all classes of compounds studied here. The procedure is described in detail only for octadecenoic acids as an example. Tables 1–5 contain data on the s values used in the evaluations. Table 6 summarizes the parameters a, b, f and z for the monounsaturated compounds.

Unsubstituted Octadecenoic Acids and Esters.—The equations for R_1 and R_2 of unsubstituted (Z)-octadecenoic acids (Fig. 1) are eqns. (4) and (5).

$$R_1 = 130.1 - (240/u^3) \qquad (4)$$

$$R_2 = 129.9 + (120/u^3) \qquad (5)$$

Subtracting eqn. (4) from eqn. (5) yields the separation of the olefinic carbons between C-3 and the POSE (Fig. 2; for data see Table 1) as eqn. (6) for data supplies by Gunstone *et al.*[5]

$$s = (360/u^3) - 0.20 \qquad (6)$$

The configuration of the double bond does not affect s. In ref.

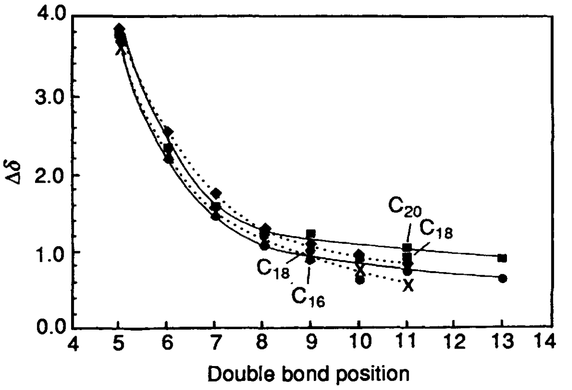

Fig. 3 Plot of the separation of the ^{13}C NMR olefinic carbon signals in octadecenoic acids and esters with position II allylic hydroxy groups *vs.* the double bond position using data provided by the authors.[9,10] Eqns. (16) and (17) approximate the observed values.

5, *s* values for *Z* and *E* unsaturation of octadecenoic acids were nearly identical for identical double bond positions (see Table 1) but the equations for R_1 and R_2 differ slightly because shift values differ for *Z* and *E* unsaturation.[5] While the signals of (*Z*)-octadecenoic acids were reported from C-3 on, the signals of the (*E*)-octadecenoic acids were reported beginning at C-5. The equations for R_1 and R_2 of the *cis* and *trans* forms are therefore only comparable with caution, especially because the R_2 value of the C-5 double bond of the (*E*)-octadecenoic acid deviates more strongly from the calculated value. In any case, equations with a better approximation for *E* configuration are (7) and (8).

$$R_1 = 130.6 - (230/u^3) \qquad (7)$$

$$R_2 = 130.4 + (130/u^3) \qquad (8)$$

The equations for unsubstituted (*Z*)-octadecenoic methyl esters (shift values given for C-2–7 and -9)[5] are (9)–(11). These

$$R_1 = 130.1 - (230/u^3) \qquad (9)$$

$$R_2 = 129.9 + (110/u^3) \qquad (10)$$

$$s = (340/u^3) + 0.2 \qquad (11)$$

equations do not take into consideration the values for the 2-ene ester, which, in contrast to the acid, were reported. The deviation for the 2-ene *s* value is relatively strong (30–40%), presumably due to the proximity to C-1.

Compounds with Allylic Hydroxy Groups.—For *E* position II allylic hydroxy acids, the equations for R_1 and R_2 are (12) and (13).

$$R_1 = 132.40 - (240/u^3) \qquad (12)$$

$$R_2 = 132.80 + (160/u^3) \qquad (13)$$

The nature of the functional group at C-1 also plays a role. In position II allylic hydroxy fatty compounds, *s* of olefinic carbon signals was greater for ester moieties at C-1 than for carboxylic acid or alcohol functionalities at C-1.[9] The differences for acids and alcohols were similar. The difference between position II allylic hydroxy fatty acids and esters is about 0.2 ppm.

The equations for R_1 and R_2 of position *E* II allylic hydroxy esters are (14) and (15).

$$R_1 = 132.30 - (240/u^3) \qquad (14)$$

Table 2 Observed and calculated separations (ppm) of the olefinic carbon shifts in position II allylic hydroxy compounds[a]

Double bond position	Acid $s_{\text{obsd.}}$	Acid $s_{\text{calcd.}}$	Ester $s_{\text{obsd.}}$	Ester $s_{\text{calcd.}}$
5	3.68	3.60	3.79	3.80
6	2.20	2.25	2.37	2.45
7	1.46	1.57	1.60	1.77
8	1.07	1.18	1.25	1.38
9	0.89, 1.00[b]	0.95	1.22, 1.29[b]	1.15
10	0.63	0.80	0.92	1.00
11	0.74	0.70	0.93, 1.05[b]	0.90
12	–	0.63	–	0.83
13	0.65	0.58	0.92	0.78

[a] The observed separations are also given in ref. 10 and actual shift data are given in refs. 9 and 10. The calculated data are approximated by eqns. (16) and (17). For a plot see Fig. 3. [b] Values obtained from different compounds. See the text.

$$R_2 = 132.90 + (160/u^3) \qquad (15)$$

The equation for *s* of position II hydroxy acids (Fig. 3; for data see Table 2) is (16) and the equation for position II hydroxy

$$s = (400/u^3) + 0.40 \qquad (16)$$

esters (Fig. 3; for data see Table 2) is (17) for data from refs. 9, 10.

$$s = (400/u^3) + 0.60 \qquad (17)$$

There is a limitation on the equations for the compounds with the allylic hydroxy groups. Similar to the above discussion of unsubstituted (*E*)-octadecenoic acids, this limitation results because the C-5 double bond is closest to the functional group. Thus, only the smaller shift differences of the olefinic carbons approaching the POSE* are considered.

Unsubstituted Octadecynoic Acids.—For unsubstituted octadecynoic acid, the two equations for R_1 and R_2 between C-2 and the POSE utilizing literature data[6] are (18) and (19).

$$R_1 = 80.45 - (30/u^2) \qquad (18)$$

$$R_2 = 79.8 + (50/u^2) \qquad (19)$$

Subtracting eqn. (18) from eqn. (19) gives *s* (Fig. 4; for data see Table 3) as eqn. (20). Contrary to the octadecenoic compounds,

$$s = (80/u^2) - 0.65 \qquad (20)$$

for octadecynoic compounds there is no significant deviation from the calculated values at the C-2 unsaturation.

Unsubstituted Octadecadienoic Acids.—Data provided by Gunstone *et al.*[5] can be used partially to evaluate all-(*Z*)-octadecadienoic acids in which one double bond is kept constant at C-12 while the other moves from C-5 to -9. A plot (Fig. 5; for data see Table 4) of the position of the double bond closer to C-1 for constant unsaturation at C-12 *vs.* *s* of C-12 is

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* The POSE in the case of allylic hydroxy acids could more accurately be termed 'position of minimal shift separation'. The olefinic carbons of the allylic hydroxy compounds will always exhibit some separation due to the proximity of the OH group (even when assuming a compound of infinite chain length with the allylic hydroxy group at its centre). This separation, however, reaches its minimum at the positions corresponding to the POSE of the unsubstituted compounds.

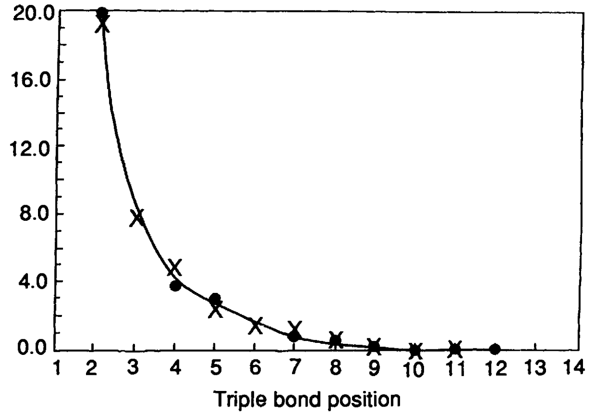

Fig. 4 Plot of the separation of the ^{13}C NMR acetylenic carbon signals in unsubstituted octadecynoic acids *vs.* the triple bond position using data obtained from Gunstone *et al.*[4] The plot depicts the function which approximates the datapoints while the datapoints for the measured values are also shown.

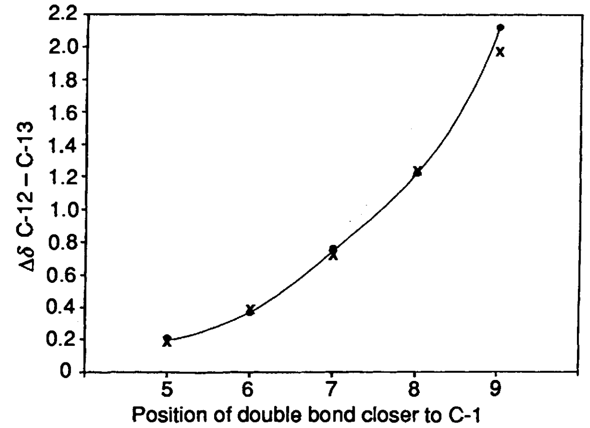

Fig. 5 Plot of the position of the double bond closer to C-1 *vs.* s of the olefinic carbons at C-12 for octadecadienoic acids in which one double bond is located at C-12–C-13 and the other double bond moves from C-5 to C-9 (shift data supplied by Gunstone *et al.*[5]). The observed values of s are approximated by eqn. (21).

Table 3 Observed and calculated separations (ppm) of the unsaturated carbon shifts in unsubstituted octadecynoic acids[a]

Triple bond position	$s_{obsd.}$	$s_{calcd.}$
2	19.90	19.35
3	—	8.24
4	3.78	4.35
5	2.97	2.55
6	—	1.57
7	0.88	0.98
8	0.52	0.60
9	0.30	0.34
10	0.17	0.15
11	0.00	0.01
12	0.00	−0.09
13	0.00	

[a] The observed separations were calculated from data in ref. 6 (for actual shift values as basis of the calculated separations, see ref. 6). The calculated data are approximated by eqn. (20). For a plot see Fig. 4.

Table 4 Observed and calculated separations (ppm) of the unsaturated carbon shifts in unsubstituted octadecadienoic acids with one double bond constant at C-12–C-13 while the other moves from C-5 to C-9[a]

Position of double bond closer to C-1	$s_{obsd.}$	$s_{calcd.}$
5	0.21	0.19
6	0.37	0.39
7	0.76	0.72
8	1.22	1.23
9	2.12	1.97

[a] The observed separations were calculated from data in ref. 5 (for actual shift values as basis of the calculated separations, see ref. 5). The calculated data are approximated by eqn. (21). For a plot see Fig. 5.

Table 5 Observed and calculated separations (ppm) of the unsaturated carbon shifts of the double bond farther from C-1 in unsubstituted octadeca-1,5-dienoic acids[a]

Position of double bond farther from C-1	$s_{obsd.}$	$s_{calcd.}$
6	3.00	2.83
7	2.20	2.35
8	1.70	2.00
9	1.60	1.72
10	1.40	1.50
11	1.35	1.32
12	1.25	1.16

[a] The observed separations were calculated from data in ref. 5 (for actual shift values as basis of the calculated separations, see ref. 5). The calculated data are approximated by eqn. (23).

approximated by the eqn. (21). The subscript *dbl* notes that u refers to the position of the double bond closer to C-1.

$$s_{12} = 0.0003u_{db1}^4 \qquad (21)$$

Eqn. (21) differs from the ones derived above because here the s of a double bond at the POSE relative to the functional group at C-1 is being considered in dependence of the relative position of another double bond.

The s of the double bond closer to C-1 (the 'migrating' bond) is influenced by both the constant double bond at C-12 and the functional group at C-1. The s of its olefinic carbons when applying eqn. (1) are, according to literature data,[5] 3.00 ppm at C-5, 1.28 ppm at C-6, 0.21 ppm at C-7, −0.62 ppm at C-8 and −0.77 ppm at C-9. There is no observed POSE in this case, although a theoretical value between C-7 and -8 could be deduced. Due to the inherent sparseness of datapoints for either side of the POSE, an equation for the separation of the olefinic carbon shifts of the double bond closer to C-1 was not determined. It is possible, however, that the signals for C-5–C-7 are inversely proportional to a power (the 4th?) of u of this double bond.

Bus *et al.*[8] gave data for all-(Z)-octadecadienoic acids with 1,5-unsaturation. The position of the double bond closer to C-1 moved from C-2 to -12 while the double bond farther from C-1 accordingly shifted from C-6 to -16. While the approximation of the olefinic shift separations of the double bond close to C-1 by an eqn. such as (22) gives larger deviations from the observed

$$s_{db1} = (300/u^3) - 1.2 \qquad (22)$$

values, the approximation of the olefinic shift separations of the double bond farther from C-1 by eqn. (23), agrees better with

$$s_{db2} = (20/u) - 0.5 \qquad (23)$$

the observed data (see Table 5).

Similar equations to those discussed here presumably exist for positions beyond the POSE where s according to eqn. (1) is negative. Due to the paucity of data for these positions and the fact that the effect is valid only for the relatively small number of positions between the POSE and the terminal methyl group, no attempt was made to determine any equations.

Table 6 Equation parameters [for eqns. (4)–(20)] as defined in the text for some monounsaturated fatty compounds (chain length C_{18})

	R_1			R_2			s		
Entry[a]	b	a	z	b	a	z	b	a	f
1 Z, CO_2H	3	−240	130.1	3	120	129.9	3	360	−0.2
2 E, CO_2H	3	−230	130.6	3	130	130.4	3	360	−0.2
3 Z, CO_2CH_3	3	—230	130.1	3	110	129.9	3	340	−0.2
4 E, CO_2H, CH=CH–CHOH	3	−240	132.4	3	160	132.8	3	400	0.4
5 E, CO_2CH_3, CH=CH–CHOH	3	−240	132.3	3	160	132.9	3	400	0.6
6 tr, CO_2H	2	−30	80.45	2	50	79.8	2	80	−0.65

[a] The following abbreviations and symbols are used in this column: tr = a triple bond; CH=CH–CHOH indicates compounds containing the allylic hydroxy group; CO_2H and CO_2CH_3 refer to the functional group at C-1.

Deviations of Calculated from Observed Values.—For some datapoints, the calculated values deviate from the observed values in ranges up to approximately ±10% (in a few cases even more). A review of literature data, however, revealed that different investigators reported differences within this range for identical or similar compounds. A few examples may illustrate this.

For evaluating unsubstituted octadecenoic acids and esters, data provided by Gunstone *et al.*[5] were utilized but similar data (all values rounded to the nearest 0.05 ppm) were also supplied by Bus *et al.*[8] In Ref. 5, the olefinic carbon shift separation of (Z)-methyl octadec-4-enoate is 4.01 ppm while the separations of (Z)-methyl dec-4-enoate and (Z)-methyl undec-4-enoate calculated from ref. 8 are 4.30 and 4.40 ppm, respectively.* From the same literature,[5,8] the separations are 2.77 and 2.90 ppm for (Z)-methyl octadec-5-enoate.

Position II allylic hydroxy compounds[9] provide other examples. The olefinic carbon shift separations are 0.89 and 1.00 ppm for (E)-11-hydroxyhexadec-9-enoic acid and (E)-11-hydroxyoctadec-9-enoic acid, respectively. For (E)-methyl 13-hydroxyoctadec-11-enoate and (E)-methyl 13-hydroxyicos-11-enoate, the separations are 0.93 and 1.05 ppm, respectively.

In light of the deviations in the observed values, it can be assumed that the equations reported here are indeed valid approximations of the observed values and are within experimental error.

Besides the values of methyl (Z)-octadecenoates,[1,5] the spectra of glycerol triesters with monoenoic chains were reported.[1] In these cases, as for the methyl esters discussed above, there is a substantial deviation of the calculated values for C-2 unsaturation from the observed values. If the equations are tailored better to approximate the C-2 value, the deviations for the C-3–C-5 values become larger. When C-2 values are not taken into account, the values from C-3 to the POSE fit the equations considerably better.

Relation to Electric Field Effects.—Batchelor *et al.*[3,4] discussed steric and electric field effects on the ^{13}C NMR spectra of unsaturated fatty compounds. For double bonds, the decrease of s (and of the component of the electric field resolved along the double bond) with increasing distance from C-1 was expected due to distance and orientation effects.[3] These authors then found by computer simulation taking into account various thermodynamical parameters that if the decrease were related to a power of the unsaturation, the best value would be −3.5. On the other hand, if the hydrocarbon chain were rigid, the orientation of the double bond relative to the dipole (*i.e.*, the functional group at C-1) would remain fixed and only distance would influence the decrease and the decrease would be proportional to the negative third power of u.[3] The negative third power of u was found in the present work for all compounds with monoalkenoic unsaturation. The literature results[3] on monoenoic compounds thus coincide with the present derivation from actual data. A completely random chain conformation would yield a dependence of $u^{-1.5}$.[3]

The present results show that the shift values and resulting separations depend on the functional group at C-1 and the nature and number of the unsaturations. At present, we do not have a satisfactory physical explanation why the s values of different unsaturations depend on different powers of u. The presence of an additional functional group, the allylic hydroxy group in position II, had comparatively little effect on the equations.

On the other hand, the resonances of octadecadienoic acids are more complicated by being proportional to different powers of u, depending also on the positions of the double bonds relative to another within the chain. We also attempted to evaluate the octadeca-1,5-diynoic acids reported by Bus *et al.*[7] but were unable to develop a satisfactory approximation. Electric field contributions to the spectra of polyunsaturated fatty acids are more complex because of the presence of the functional group at C-1 and the other unsaturation(s).[4] The deviations of the calculated from the observed values discussed above might therefore be interpreted in terms of the electric field model.

Solvents can influence the effects discussed here.[3,4] There should, however, be no solvent effect in the present evaluation because apparently all spectra were obtained with $CDCl_3$ as solvent.

Conclusions

Rational functions giving approximations of the chemical shifts of olefinic carbons between C-1 and the POSE were obtained. Previously, these signals had been evaluated by additive or subtractive increments relative to a standard.[1–4] The present approach may present another opportunity for describing the multitude of effects on the shifts. The chemical shifts of the unsaturated carbons are proportional or inversely proportional to the first, second, third, or fourth powers of the position of the unsaturation depending on the other functional groups in the molecule and the nature of the unsaturation.

Table 6 summarizes the data for C_{18} monounsaturated fatty acids.

References

1 F. D. Gunstone, High Resolution ^{13}C NMR Spectroscopy of Lipids, in *Advances in Lipid Methodology—Two*, ed. W. W. Christie, The Oily Press, Dundee, 1993, pp. 1–68 and ref. therein.

2 P. E. Hansen, 'Nuclear Magnetic Resonance Spectroscopy of C=C, C=O, C=N and N=N Double Bonds', in *The Chemistry of Double-bonded Functional Groups*, ed. S. Patai, Wiley, Chichester, 1989, vol. 2, Part. 1, pp. 81–162 and refs. therein.

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* Although the compounds compared here have different chain lengths, the double bond is sufficiently remote from the terminal methyl group. Also, s values for C-5 unsaturation of the corresponding methyl esters of C_{11}, C_{14} and C_{18} chain lengths are identical in ref. 8.

3 J. G. Batchelor, J. H. Prestegard, R. J. Cushley and S. R. Lipsky, *J. Am. Chem. Soc.*, 1973, **95**, 6358.

4 J. G. Batchelor, R. J. Cushley and J. H. Prestegard, *J. Org. Chem.*, 1974, **39**, 1698.

5 F. D. Gunstone, M. R. Pollard, C. M. Scrimgeour and H. S. Vedanayagam, *Chem. Phys. Lipids*, 1977, **18**, 115.

6 F. D. Gunstone, M. R. Pollard, C. M. Scrimgeour, N. W. Gilman and B. C. Holland, *Chem. Phys. Lipids*, 1976, **17**, 1.

7 J. Bus, I. Sies and M. S. F. Lie Ken Jie, *Chem. Phys. Lipids*, 1976, **17**, 501.

8 J. Bus, I. Sies and M. S. F. Lie Ken Jie, *Chem. Phys. Lipids*, 1977, **18**, 130.

9 G. Knothe, M. O. Bagby, D. Weisleder and R. E. Peterson, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1661.

10 G. Knothe, M. O. Bagby, D. Weisleder and R. E. Peterson, submitted for publication.

11 (*a*) P. E. Pfeffer, P. E. Sonnet, D. P. Schwartz, S. F. Osman, D. Weisleder, *Lipids*, 1992, **27**, 285; (*b*) a paper revising the assignments of the olefinic carbon signals in ref. 11(*a*), M. S. F. Lie Ken Jie and A. K. L. Cheng, *Nat. Prod. Lett.*, 1993, **3**, 65 (we thank Drs. F. D. Gunstone and P. E. Sonnet for calling our attention to this paper); (*c*) homoallylic and bis-homoallylic hydroxy fatty compounds were not selected for evaluation because the values in ref. 11(*a*) are mainly predicted. Actual data for these compounds are too sparse for evaluation.

12 J. Bus and D. J. Frost, 'Determination of the Positions of Double Bonds in Unsaturated Fatty Acids by ^{13}C and Proton NMR Spectrometry', in *Lipids, Vol. 2: Technology*, eds. R. Paoletti, G. Jacini and R. Porcellati, Raven Press, New York, 1976, pp. 343–350.

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