

The Composition of Hydrogenated Fats by High-Resolution ^{13}C Nuclear Magnetic Resonance Spectroscopy

Frank D. Gunstone

Chemistry Department, The University, St. Andrews, Fife, KY16 9ST, Scotland

The high-resolution ^{13}C nuclear magnetic resonance spectra of twelve hydrogenated fats have been examined. Each spectrum contains 50–100 signals and reveals much about the nature of the acyl chains of both double-bond position and configuration. The signals for the ω_1 , ω_2 and ω_3 carbon atoms give information on the *cis* and *trans* isomers of the Δ_{15} , Δ_{14} , Δ_{13} and Δ_{12} 18:1 esters, respectively. Allylic signals distinguish between *cis* and *trans* esters, and the proportion of total *cis* to total *trans* isomers can be obtained from these. Olefinic signals are the most informative, and most of these have been assigned. This leads to a semi-quantitative estimate of the various 18:1 isomers present. Assignments are based mainly on information already in the literature, but some were confirmed after urea fractionation of the acids from a hydrogenated oil in which *cis* and *trans* monoene acids were separately concentrated.

KEY WORDS: *cis/trans* spectroscopy, double-bond migration, hydrogenated fats, ^{13}C NMR spectroscopy, positional isomers (in hydrogenated fats), urea fractionation.

To extend the use of natural fats and to improve on their properties—especially their melting behavior—lipid chemists and technologists have exploited a number of procedures. Those most commonly employed include fractionation, interesterification and partial hydrogenation. The latter, while raising melting point and modifying melting behavior, also reduces the content of methylene-interrupted polyene acids and so enhances oxidative stability. However, these improvements are achieved at the cost of reducing the level of essential fatty acids and of producing acids that are either unnatural or occur only rarely and at low levels in natural sources. This arises because, in partial hydrogenation, saturation of some double bonds is accompanied by stereomutation (change of lower-melting *cis* isomers to higher-melting *trans* isomers) and by double-bond migration of others.

Because of these changes, partially hydrogenated fats are complex in terms of their fatty acids and even more so in respect of their glycerides, and the analyses of such fats presents a formidable challenge. Stereoisomers and positional isomers cannot yet be fully resolved by gas chromatographic procedures (1–3). The *trans* isomers in total are determined spectroscopically (infrared) or chromatographically, but, because there is no simple way to detect and quantitate positional isomers, they are usually ignored.

Nevertheless, double-bond position has a minor influence on melting point, as indicated by the figures in Table 1 showing the melting points of the *cis* and *trans* isomers of the Δ_7 to Δ_{14} acids.

Continuing our study of the application of high-resolution nuclear magnetic resonance (NMR) spectroscopy to fatty acids and their derivatives, we have now examined some synthetic glycerides containing oleic and/or elaidic acid and several partially hydrogenated fats.

TABLE 1

Melting Points ($^{\circ}\text{C}$) of Some *cis* and *trans* Octadecenoic Acids (Ref. 4)

Double-bond position	7	8	9	10	11	12	13	14
<i>cis</i>	13	24	11	23	13	28	27	42
<i>trans</i>	45	52	45	53	44	53	44	53

We find the ^{13}C spectra to provide a good deal of useful information (5,6).

In addition to the methylene envelope (peaks with chemical shift 29.1–29.8 ppm, which cannot be completely and easily assigned), the spectra contain easily recognized signals for: (i) glycerol or other alcohol components of an ester; (ii) the C1, C2 and C3 atoms, which often furnish two signals corresponding to the α - and β -chains; (iii) the ω_1 , ω_2 and ω_3 atoms, which may provide information about nearby double bonds; and (iv) olefinic and allylic carbon atoms, which give useful information about the position and configuration of double bonds. In the spectrum of a single molecular species, the signals appear as single or double resonances (α - and β -chains). However, with mixtures, whether native or modified, these simple signals are replaced by clusters with similar, but not identical, chemical shifts. Understanding these clusters provides valuable information about the mixture under examination.

EXPERIMENTAL PROCEDURES

Synthetic glycerides containing elaidic acid (SSE, SES, PES, ESE, EPE, SEE, SEO and SOE; P, palmitic acid; S, stearic acid; E, elaidic acid; and O, oleic acid) were kindly supplied by R.P. Potman (Unilever Research, Vlaardingen Laboratory, Vlaardingen, The Netherlands). F.B. Padley (Unilever Research, Colworth Laboratory, United Kingdom; samples A–D), C. Bagge (Karlshamns, Karlshamn, Sweden; samples E–J) and V.K.S. Shukla (IFSC, Lystrup, Denmark; samples K and L) supplied hydrogenated oils. Among these was a set of rapeseed oils hydrogenated to melting points of 5, 12, 40, 41 and 43°C (F–J).

Our spectra were measured with a Bruker AM 300 spectrophotometer (pulse angle 51° , pulse repetition time 1.82 s, resolution 1.22 Hz per data point) in solutions of CDCl_3 .

Two of the fats were hydrolyzed with aqueous ethanolic alkali, and the recovered acids were crystallized from urea and methanol. Fatty acids were recovered from both the adduct and the mother liquor (7).

RESULTS AND DISCUSSION

Assignment of chemical shifts. The assignment of the many signals (50–100) in these hydrogenated oils has been greatly facilitated by the results from synthetic *cis* and *trans* octadecenoic acids already reported by Gunstone

et al. (8) in 1977. In that study almost all the isomeric 18:1 acids were examined, but unfortunately no mixtures were investigated, and from the results cited there it is not possible to know how far small differences in chemical shifts are due to experimental variation and how far they are real and reproducible. An examination of the figures as given in the 1977 paper for the $\Delta 5$ - $\Delta 15$ acids suggests the following four conclusions:

Each isomer has its own olefinic signals (usually two). These differ between the *cis* and *trans* isomers and with the position of the double bond. As a double bond gets further from the carboxyl group, its two olefinic signals get closer together and merge into one for the $\Delta 12$ and $\Delta 13$ isomers. Thereafter, the signals separate into two again. Values taken from the earlier paper are set out in Table 2. In using these values to make assignments, it is important to note both the difference between the two chemical shifts for each isomer and the difference in shift between adjacent isomers. The values observed in this study with triolein, trielaidin, and with methyl *cis* and *trans* vaccenates are also in Table 2. These provide a useful starting point for the assignment of olefinic signals.

Allylic signals normally lie within the range 27.3-27.4 and 32.6-32.7 ppm for *cis* and *trans* isomers, respectively.

Additional values falling outside this range may be indicators of the presence of these isomers: 29.69 (14*c*), 27.21 and 20.60 (15*c*), 27.13 (7*c*), 26.99 (13*c*), 26.88 (6*c*) and 26.58 ppm (5*c*), and at 34.79 (14*t*), 32.40 (7*t*), 32.36 (13*t*), 32.21 (6*t*), 31.91 (5*t*), and 25.65 ppm (15*t*).

Each double bond also exerts a smaller, but significant, influence on methylene groups in the γ -position, with the usual chemical shifts being reduced between 0.3 and 0.7 ppm. The effect is larger for the *trans* double bond—usually by about 0.15 ppm. The effect of double bonds on the signals at C2, C3 and $\omega 1$ -3 are set out in Table 3.

The methylene envelope usually covers the range 29.1-29.8 ppm. Some of the carbon atoms that give signals at the lower end of this range (C4-C6 and C15) in stearic acid give lower values when associated with double bonds in appropriate positions. The 1977 figures (8) show ten signals with values below 29.1, some of them markedly so. They are: 28.63 (C4, 7*t*), 28.79 (C5, 8*t*), 28.88 (C4, 7*c*), 28.93 (C15, 11*t*), 28.96 (C5, 8*c*), 29.00 (C6, 9*t*), 29.02 (C4, 8*t*), 29.07 (C4, 6*t*), 29.08 (C4, 8*c*) and 29.08 (C15, 11*c*). In seven of these ten signals the double bond is γ - to the carbon atom in question.

Synthetic compounds. In a preliminary experiment, the spectra of glycerol trioleate (OOO), glycerol trielaidate

TABLE 2

Chemical Shifts (ppm) for *cis* and *trans* Olefinic Carbon Atoms in 18:1 Isomers (Ref. 8)^a

<i>trans</i>				<i>cis</i>			
5	131.98 (0.85) ^c	128.72 (0.77)	[3.26] ^b	5	131.44 (0.82)	128.21 (0.80)	[3.23]
6	131.13 (0.32)	129.49 (0.40)	[1.64]	6	130.62 (0.31)	129.01 (0.44)	[1.61]
7	130.81 (0.14)	129.89 (0.24)	[0.92]	7	130.31 (0.14)	129.45 (0.20)	[0.86]
8	130.67 (0.13)	130.13 (0.10)	[0.54]	8	130.17 (0.08)	129.65 (0.13)	[0.52]
9	130.54 (0.07)	130.23 (0.08)	[0.31]	9	130.09 (0.09)	129.78 (0.05)	[0.31]
10	130.47 (0.04)	130.31 (0.03)	[0.16]	10	130.00 (0.04)	129.83 (0.06)	[0.17]
11	130.43	130.34	[0.09]	11	129.96	129.89	[0.07]
12		130.14		12		129.94	
13		130.39		13		129.90	
14	130.63	130.13	[0.50]	14	130.16	129.66	[0.50]
15	131.93	129.45	[2.48]	15	131.54	129.39	[2.15]

^aIn the present study, olefinic chemical shifts of 130.50 and 130.19 (trielaidin), 130.40 and 130.32 (methyl *trans*-vaccenate), 130.02 and 129.71 (triolein), and 129.93 and 129.85 (methyl *cis*-vaccenate) were observed for the esters named.

^bNumbers in brackets are the differences between values (horizontal), the two olefinic signals for each acid.

^cNumbers in parentheses are the differences between values (vertical), adjacent isomers.

TABLE 3

Effect of Double Bonds γ to the C2, C3 and $\omega 1$ - $\omega 3$ Carbon Atoms (Ref. 7)

	<i>cis</i>			<i>trans</i>			Double-bond position
	range (ppm)	γ	α^a	range (ppm)	γ	α	
C2	34.18-34.25	33.58	(0.64)	34.19-34.22	33.47	(0.74)	$\Delta 5$
C3	24.74-24.81	24.39	(0.39)	24.74-24.78	24.22	(0.54)	$\Delta 6$
$\omega 3$	32.01-32.10	31.64	(0.42)	32.00-32.05	31.49	(0.54)	$\Delta 12$
$\omega 2$	22.72-22.82	22.40	(0.37)	22.73-22.78	22.27	(0.49)	$\Delta 13$
$\omega 1$	14.09-14.13	13.80	(0.31)	14.07-14.12	13.64	(0.46)	$\Delta 14$

^aThe α equals the difference between the quoted value and the average value of the range.

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(EEE), and a weighed mixture of these two were examined. We have also examined a number of other synthetic glycerides alone and as mixtures. These include SSE, SES, PES, ESE, EPE, SEE, SEO and SOE.

From the spectra of these compounds and their mixtures it was clear that: (i) Signals for the olefinic carbon atoms of elaidic esters (130.49 and 130.18 ppm) are well separated from those of oleic esters (130.00 and 129.70 ppm). When the spectra are submitted to resolution enhancement, the signals for E9 and O9 split into two, representing α - and β -chains, but the E10 and O10 signals are not usually resolved. (ii) The allylic carbon atoms give signals that are quite distinct for elaidic (32.63 and 32.58 ppm) and oleic esters (27.24 and 27.19 ppm). (iii) There were small, but significant, differences in the signals of the methylene envelope for oleic esters (signals at 29.79 and 29.73 ppm, absent from elaidic esters) and elaidic esters (signals at 29.10, 29.07 and 28.99 ppm, absent from the oleic esters) (see Table 4).

These observations were extended to a mixture of oleic- and elaidic-containing glycerides to which the *cis* and *trans* isomers of methyl vaccenate ($\Delta 11$) had been added. This mixture showed eight olefinic signals corresponding to elaidate (130.50 and 130.19 ppm) oleate (130.02 and 129.71 ppm), *trans*-vaccenate (130.40 and 130.32 ppm) and *cis*-vaccenate (129.93 and 128.85 ppm).

From the intensities of both the olefinic and allylic signals, it is possible to estimate the composition of a mixture of OOO and EEE. It contained the following amount of EEE: 45.8% by weight, 45.4% from the intensity of the allylic signals and 45.6% from the intensity of the olefinic signals.

Partially hydrogenated oils. The twelve samples of hydrogenated fat (A-L) obtained from three sources (see Experimental Procedures section) were random samples, except for the five rapeseed oils (F-J) hydrogenated to different melting points. Comparison of the spectra of the

twelve samples show major signals common to all and minor signals, which appear in some, but not all, the spectra. We discuss the more important signal clusters to see what can be discovered from each.

Carbon 2. This carbon atom shows characteristic signals at 34.22 ± 0.01 and 34.07 ± 0.01 ppm, with the second signal being twice the intensity of the first. These signals correspond to the C2 atoms in the β - and α -chains, respectively, with no structural feature other than the glycerol unit to affect the shifts. A signal at 34.72 ppm is a *trans* allylic signal (C16, also $\omega 3$) and is not from C2. Sample J was interesting in that, in addition to the two major signals, it had signals at 33.90 and 33.82 ppm, corresponding to 4.1 and 1.9% of the total C2 signal. Because of the difficulty of comparing chemical shifts for this carbon atom of the acid (8) with those of glycerol esters, they cannot be assigned with certainty. They may result from $\Delta 5$ acids which would only be present in an extensively isomerized fat.

Carbon 3. Although C3 signals also differ in the α - and β -chains, the difference in chemical shift is so small that they are usually separated only after resolution enhancement. The major C3 signal (24.89 ± 0.02 ppm) is the only signal observed in eight of the spectra. In the remaining four there are also one or more minor signals at 25.10, 24.79, 24.75, 24.67 and 24.35 ppm. Sample J again provides an interesting spectrum in this region. Three minor peaks account for about 20% of this cluster: 24.89 (79.5%), 24.79 (9.4%), 24.75 (7.6%) and 24.35% (3.5%). This is evidence of double bonds close enough to this carbon atom to influence its chemical shift. The signal at 24.35 (0.54 ppm lower than the major C3 signal) probably results from the 6*t* isomer. It is not yet possible to assign the other minor signals, each of which may be associated with more than one isomer.

$\omega 1$ - $\omega 3$ Signals. More information can be derived from the $\omega 1$ - $\omega 3$ signals. The chemical shifts are unlikely to be

TABLE 4

Major Signals (chemical shift, ppm) in the Spectra of OOO and EEE and a Mixture of These Two^a

	OOO	EEE	Mixture		OOO	EEE	Mixture
C1 α	173.20	173.23	173.21	E10	—	130.49	130.48
C1 β	172.80	172.82	172.80	E9	—	130.18	130.17
				O10	130.00	—	130.00
C2 β	34.20	34.21	34.20	O9	129.70	—	129.70
C2 α	34.04	34.05	34.04				
				Methylene envelope			
C3	24.87	24.88	{ 24.90 24.87				
$\omega 1$	14.13	14.12	14.13		29.79	—	29.79
					29.73	—	29.73
					—	29.68	29.68
$\omega 2$	22.71	22.70	22.71		—	29.61	29.61
					29.36	29.34	29.36
$\omega 3$	31.94	31.93	31.94		29.21	29.21	29.22
					29.13	29.15	29.14
					—	29.10	} 29.12
E11	—	32.63	32.64		—	29.07	
E8	—	32.58	32.59		—	28.99	28.99
O11	27.24	—	27.24				
O8	27.19	—	27.19				

^aSimilar chemical shifts were observed with the synthetic elaidic glycerides. OOO, triolein acid; EEE, trielaidin.

influenced by the glycerol unit, so the values obtained from the earlier study of the acids (8) provides useful information, and the presence of linoleic acid ($\Delta 9,12$) and possibly linolenic acid ($\Delta 9,12,15$) in the oils being hydrogenated will result in double bonds closer to the methyl group than to the carboxyl group.

Apart from sample K, which shows two major signals at 14.14 and 14.12 ppm, the remainder show one principal $\omega 1$ signal at 14.12 ± 0.02 ppm and one or more minor signals at 14.40, 14.35, 14.29, 13.98 and 13.66 ppm. The signal at 14.40 appears only in sample F (2.5% of total cluster) and sample G (3.0% of total cluster). These are rapeseed oils lightly hydrogenated to melting points of 5 and 12°C, and the signal indicates a 15*c* double bond. This is present in linolenic acid and in any of its hydrogenation products that still have this double bond in this configuration. The signal at 13.66 ppm indicates 14*t* unsaturation and appears only in samples D (2.7%) and J (2.1%).

The $\omega 2$ cluster has a dominant signal at 22.71–22.73 ppm and a larger number of minor signals. The signal at 20.53 ppm, only apparent in sample F, is again indicative of 15*c* unsaturation, while those at 22.37 and 22.21 (0.35 and 0.51 ppm lower than the major signal) belong to the 13*c* and 13*t* isomers, respectively (the γ -shift). The 22.37 signal appears only once, but the 22.21 signal is observed in the spectra of seven of the twelve samples.

The $\omega 3$ cluster, with its dominant signal at 31.93–31.96 ppm, provides more information because it is getting closer to double-bond positions likely to be important. Five minor signals were noted, of which two correspond to the 12*c* (31.56) and 12*t* (31.43 ppm) isomers. These values are 0.39 and 0.52 ppm lower than the major value and are present in almost all the spectra. It is interesting that in samples F–J, which are rapeseed oils hydrogenated to higher melting points, there is a steady fall in the content of the 12*c* esters and a rise in the level of their *trans* isomers (Table 5). This is consistent with the increased level of hydrogenation through this sequence. The kind of information that can be obtained from the $\omega 1$ – $\omega 3$ signals is summarized in Table 5. It should be possible to add to this when other minor signals can be assigned with more certainty.

Allylic signals. For the most part, the *cis* and *trans* allylic signals are well separated. The former appear at 27.45, 27.40, 27.25*, 27.21*, 27.00 (13*c*), 26.94, 25.66 and 25.09 ppm, and the latter at 34.74 (14*t*), 32.86, 32.77, 32.62*, 32.55, 32.38 (7*t* and/or 13*t*), 32.30, 32.18 (6*t*), 32.05 and 25.64 (15*t*). Some of the minor signals are only provisionally identified, and major signals are marked with an asterisk. By using the intensities of all the *trans* and all the *cis* allylic signals, it is possible to calculate the proportion of *cis* and *trans* unsaturated acids. The percentage of *trans* isomers in the 12 hydrogenated oils is 66(A), 75(B), 85(C), 80(D), 81(E), 14(F), 16(G), 69(H), 82(I), 82(J), 74(K) and 18(L). The balance of the unsaturated acids are *cis* isomers. Three samples (F, G and L) have a low proportion of *trans* acids. In most of the remainder, the *trans/cis* ratio has reached or is close to the equilibrium value of 80:20. The absolute level of *cis* and *trans* acids can only be obtained if the content of saturated acids is obtained independently, as by gas chromatography.

Olefinic signals. The twelve hydrogenated fats showed 10–21 olefinic signals in their NMR spectra, and after resolution enhancement this rose to 12–25. Additional signals result either because two signals of similar shift from different isomers have been separated or by splitting due to carbon atoms in the α - or β -chains of triacylglycerols. Because resolution-enhanced spectra cannot be used, even semi-quantitatively, attention was directed to the original spectra. Most of the signals were repeated in each spectrum and, ignoring some signals found only in the three lightly hydrogenated oils (possibly dienes or trienes), 23 different signals were present in the 12 spectra.

These are listed in Table 6 along with the number of times they appear in the 12 spectra and a possible assignment. Most of these are probably correct, but some overlapping signals have not been fully assigned. The signals for oleic (9*c*) and elaidic (9*t*) esters are easily identified, and the others follow on the basis of the information already discussed. It is known, for example, that the 10*c*–13*c* isomers will have signals lying between these for the 9*c* isomer and the same is true in the *trans* series. Signals for the *trans* $\Delta 8$, $\Delta 7$, $\Delta 6$, etc., esters lie outside those identified as belonging to the 9*t* isomer. As already indicated, attention is given to the difference between the

TABLE 5

Information Derived from the $\omega 1$ – $\omega 3$ Signals (% of total cluster)

Signal (ppm) 18:1 isomer	$\omega 1^a$		$\omega 2^a$			$\omega 3^a$	
	14.40 15 <i>c</i>	13.66 14 <i>t</i>	22.37 13 <i>c</i>	22.21 13 <i>t</i>	20.53 15 <i>c</i>	31.56 12 <i>c</i>	31.43 12 <i>t</i>
Sample A	—	—	—	4.6	—	5.9	9.5
B	—	—	—	1.2	—	1.9	2.8
C	—	—	—	—	—	—	6.3
D	—	2.7	1.6	5.6	—	3.6	10.2
E	—	—	—	5.1	—	4.0	8.5
F	2.5	—	—	—	2.2	12.9	2.3
G	3.0	—	—	—	—	10.6	2.8
H	—	—	—	—	—	3.2	5.2
I	—	—	—	3.2	—	3.4	7.5
J	—	2.1	—	4.4	—	3.4	7.5
K	—	—	—	—	—	—	2.3
L	—	—	—	0.6	—	3.3	2.1

^aMajor signal: $\omega 1$, 14.12; $\omega 2$, 22.72; $\omega 3$, 31.95 ppm.

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TABLE 6

The Chemical Shift (frequency of occurrence) and Assignment of Olefinic Signals Observed in Twelve Hydrogenated Fats

ppm	Assignment	ppm	Assignment	ppm	Assignment
131.85 (1)	5 <i>t</i>	130.25 (10)	10 <i>t</i>	129.78 (5)	10 <i>c</i>
131.05 (1)	6 <i>t</i>	130.18 (12)	9 <i>t</i>	129.70 (12)	9 <i>c</i>
130.74 (9)	7 <i>t</i>	130.09 (6)	8 <i>c</i> , 8 <i>t</i>	129.58 (6)	8 <i>c</i>
130.59 (12)	8 <i>t</i> , 14 <i>t</i>	130.04 (2)	14 <i>c</i> , 14 <i>t</i>	129.55 (1)	—
130.49 (12)	9 <i>t</i>	130.02 (12)	9 <i>c</i>	129.41 (2)	6 <i>t</i>
130.43 (11)	10 <i>t</i>	129.95 (5)	10 <i>c</i>	129.37 (3)	—
130.40 (7)	11-13 <i>t</i>	129.92 (6)	11-13 <i>c</i>	128.64 (1)	5 <i>t</i>
130.30 (9)		129.83 (12)	7 <i>t</i>		

chemical shifts for each isomer and to the differences between adjacent isomers. The intensity data can be used to obtain semi-quantitative estimates, and the results for selected examples are given in Table 7.

Three of the oils (F, G and L) are lightly hydrogenated. This is apparent from: (i) the limited range of olefinic signals, (ii) the low intensity of most of these; (iii) the fact that *cis* isomers exceed those in the *trans* form; (iv) the high intensity of the signals for oleate; and (v) the presence of the four olefinic signals associated with linoleate (9*c*,12*c*). One example is included in the selection given in Table 7.

In spectra run over a longer period of time (kindly carried out by Unilever Research), additional signals were observed, and in the spectra of D no less than 47 signals appeared. This permitted recognition of the following double bonds: *cis*: 7, 8/14, 9, 10, 11, 12/13, 15; *trans*: 5, 6, 7, 8/14, 9, 10, 11, 12/13, 15. The Δ 9, 10 and 11 isomers—both *cis* and *trans*—showed two signals for one of their olefinic carbon atoms relating to the α - and β -chains.

Methylene envelope. The hydrogenated oils show signals at 29.00, 28.87, 28.77 and 28.62 ppm outside the usual methylene envelope range (29.1-29.8), but we have made no attempt to assign these.

Urea fractionation. To confirm and extend the assignment of the olefinic signals, two of the hydrogenated oils

(D and J) were converted to acids and then separated by urea fractionation into an adduct (enriched in saturated and *trans* monoene acids) and a mother liquor (enriched in *cis* monoene acids). By using acids, it was easier to correlate chemical shifts with those previously reported (8), and splits for α - and β -chains were absent. The spectroscopic results for one example are set out in Table 8. In addition to the concentration of the various categories of acids indicated above, the distribution of the *trans* acids was interesting in that the Δ 8, Δ 10 and Δ 12 acids are more effectively included in the adduct than their Δ 7, Δ 9 and Δ 11 isomers. We do not have an explanation for this.

TABLE 8

Olefinic Signals, Assignments and Percentages of Total Intensity for Olefinic Signals for Acids from Hydrogenated Oil J and from the Urea Adduct and Liquor

ppm	Assignment	Acids	Liquor	Adduct
140.67	—	—	0.4	—
132.27	—	—	—	0.4
131.93	5 <i>t</i>	0.8	0.8	0.8
131.87	—	1.1	—	0.9
131.71	—	—	—	0.5
131.10	6 <i>t</i>	2.3	—	2.8
130.78	7 <i>t</i>	3.6	5.2	3.2
130.61	8 <i>t</i> ,14 <i>t</i>	7.2	3.3	8.7
130.51	9 <i>t</i>	7.7	5.6	6.8
130.46	10 <i>t</i>	8.8	—	10.2
130.41	} 11-13 <i>t</i>	8.7	2.2	10.5
130.33		10.8	2.7	12.9
130.28	10 <i>t</i>	8.9	4.0	11.0
130.21	9 <i>t</i>	6.8	6.4	7.3
130.13	} 8 <i>c</i> , <i>t</i>	4.3	8.0	—
130.09		14 <i>c</i> , <i>t</i>	6.7	—
130.03	9 <i>c</i>	—	6.1	2.6
129.98	10 <i>c</i>	3.6	8.5	—
129.94	} 11-13 <i>c</i>	3.4	8.4	—
129.87		7 <i>t</i>	6.7	11.9
129.81	10 <i>c</i>	—	7.8	—
129.74	9 <i>c</i>	2.5	5.2	1.4
129.61	8 <i>c</i>	2.2	6.7	0.6
129.48	—	—	—	2.7
129.41	7 <i>c</i> ,6 <i>t</i>	2.5	2.5	1.7
128.97	6 <i>c</i>	0.6	2.1	—
128.70	—	—	—	0.9
128.64	5 <i>t</i>	0.8	1.2	—
124.78	—	—	—	0.4
121.78	—	—	1.0	—
104.50	—	—	—	0.6

TABLE 7

18:1 Isomer Distribution in Selected Samples (based on olefinic signals)^a

Acid	D	E	F	J
18:1 5 <i>t</i>	—	—	—	2.3
6 <i>t</i>	1.3	—	—	4.8
7 <i>t</i>	3.4	4.0	—	7.6
8 <i>t</i>	10.4	10.0	2.4	13.8
9 <i>t</i>	17.0	17.2	5.0	13.7
10 <i>t</i>	21.9	23.2	3.6	15.5
11-13 <i>t</i>	26.0	26.2	15.2	18.3
14-15 <i>t</i>	—	—	—	3.4
8 <i>c</i>	3.0	—	—	3.4
9 <i>c</i>	7.9	9.4	64.8	7.2
10 <i>c</i>	—	—	—	7.2
11-13 <i>c</i>	9.1	10.0	—	2.8
Linoleic	—	—	9.0	—
Total <i>trans</i>	80.0	80.6	—	79.4
Total <i>cis</i>	20.0	19.4	—	20.6

^aD, Commercial material; E, cottonseed; F, rapeseed (m.p. 5°C); J, rapeseed (m.p. 43°C).

The spectrum of a hydrogenated oil contains a large number of signals, and we have been able to assign most of these either in part or completely and to thus gain some insight into double-bond position in both the *cis* and *trans* isomers. This increased knowledge of the nature of a hydrogenated product can also be used to examine more carefully the effect of varying all the experimental conditions in terms of stereomutation and double-bond migration. It is, however, desirable to confirm our assignments and to develop procedures for producing the spectra so as to give improved quantitation. We have been informed that appropriate synthetic glycerol esters are now being prepared (Lie Ken Jie, M.S.F., personal communication).

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