Heat Treatment of Vegetable Oils. II. GC-MS and GC-FTIR Spectra of Some Isolated Cyclic Fatty Acid Monomers

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Gas liquid chromatography coupled with mass spectrometry (GC-MS) showed that the cyclic fatty acid monomers (CFAM) isolated from a heated linseed oil have two ethylenic bonds, while the CFAM isolated from heated sunflower oils were saturated and monoethylenic isomers. GC-MS studies also showed the presence of cyclohexenic derivatives in the case of linseed oil.

GLC coupled with Fourier transform infrared spectrometry (GC-FTIR) studies indicated that the CFAM isolated from linseed oil were of *cis* (Z), *trans* (E) structures except two components which were *cis,cis* (Z,Z) dienoic acids. The unsaturated CFAM isolated from sunflower oils were *cis* (Z) and *trans* (E) monoethylenic isomers. For sunflower oils, the major CFAM were isomers having a *cis* (Z) ethylenic bond. The saturated CFAM isolated from a heated sunflower oil had molecular weights of 296 and 294. The latter could correspond to some bicyclic isomers.

Fractions containing 97–99% of cyclic fatty acid monomers have been isolated from heated linseed and sunflower oils (1,2). A combination of column chromatography, urea adduct fractionation and high performance liquid chromatography (HPLC) was used to isolate these components.

In order to know the structure of a cyclic fatty acid, one has to determine the size of the ring, the nature of the substituents, the degree of unsaturation and the position and geometry of the ethylenic bonds. The size of the ring and the nature of the substituents usually are determined by gas liquid chromatography coupled with mass spectrometry, GC-MS (3–9) after total hydrogenation on platinum oxide. The position of the ethylenic bonds can be determined by GC-MS of the trimethylsilyl (TMS) derivatives (10). We are reporting the determination of the degree of unsaturation of the isolated cyclic fatty acid monomers by GC-MS and the geometry of the ethylenic bonds by GC coupled with Fourier transform infrared spectrometry (GC-FTIR). The cyclic fatty acid monomers isolated from a heated linseed oil appeared to have two ethylenic bonds, while the cyclic fatty acid monomers isolated from heated sunflower oils were saturated and monoethylenic isomers. The CFAM isolated from linseed oil were of *cis* (Z), *trans* (E) structures except for two components. Both *cis* (Z) and *trans* (E) monoethylenic CFAM were found in fractions isolated from sunflower oils.

MATERIALS AND METHODS

Gas liquid chromatography-mass spectrometry (GC-MS). All the GC-MS analyses were performed using a Ribermag R10-10C quadrupole mass spectrometer coupled to a Girdel 31 gas chromatograph fitted with a split-splitless injector and a Chrompack fused-silica capillary column (26 m × 0.32 mm i.d., stationary bonded phase: 1.2 μm of CpWax 57 CB). Helium was used as the carrier gas at a flow rate of one ml/min. The injection port was maintained at 240 C, and splitless injections (1 μl) of hexane solutions were used.

The transfer line, consisting of a deactivated fused-silica capillary column (50 cm × 0.32 mm i.d.) connected to the analytical column with a zero-dead volume capillary butt-connector (Supelco Inc., Bellefonte, Pennsylvania), maintained at 280 C, was connected directly to the ion source of the spectrometer. Oven temperatures were programmed from 80 to 220 C at 10 C/min, and then held isothermally for completion of the analyses.

Mass spectra were obtained on a 0.8-sec cycle, the instrument scanning from 25 to 300 a.m.u., the energy of the ionizing electrons was 70 eV and temperature of the ionization chamber 150 C.

Gas chromatography-Fourier transform infrared spectrometry (GC-FTIR). All GC-FTIR data were collected with a Bruker IFS 85 Fourier transform infrared spectrometer. This was connected using a Bruker GC-IR interface to a Carlo-Erba 5160 gas chromatograph equipped with an on-column injector and a flame ionization detector. The same CpWax 57 CB capillary column as above was used, with a helium flow rate of 2 ml/min. Two μl of the 10-fold concentrated hexane solutions were injected and oven temperatures programmed from 50 to 80 C at 30 C/min, from 80 to 220 C at 10 C/min, and then isothermally held until the analyses were completed.

The interface consisted of a gold-coated lightpipe (36 cm × 1.5 mm i.d.) maintained at 250 C. The column was extended using a zero-dead volume butt-connector (Supelco Inc., Bellefonte, Pennsylvania) and a deactivated fused silica capillary column (50 cm × 0.32 i.d.), and this was fed through the heated transfer line up to the entrance of the lightpipe. Nitrogen make-up gas was introduced into the transfer line to reduce peak broadening within the lightpipe, resulting in a total gas flow rate of 8 ml/min.

Using the standard Bruker software, 12 interferograms were collected per second at 8 cm^{-1} spectral resolution, and three interferograms were co-added in real time, resulting in four effective spectra per second. A narrow band (4800 to 600 cm^{-1}) mercury-cadmium-telluride (MCT) detector was used.

RESULTS AND DISCUSSION

Infrared spectra of oleic and elaidic acids. Infrared spectroscopy is a dedicated spectroscopic method to distinguish *cis* (Z) and *trans* (E) isomers. It has been used extensively in the lipid field especially to determine the amount of *trans* (E) unsaturated fatty acids in partially hydrogenated oils (11). Infrared spectra obtained in the vapor phase are rather different from those obtained in the traditional condensed phase (12). However, the possibility of obtaining on-line infrared spectra of peaks eluting from a chromatograph on a GC-FTIR system, without further separation and purification, is an obvious advantage (13–15).

Very good GLC separations of the cyclic fatty acid monomers were obtained on capillary columns coated with polar liquid phases such as SILAR-10C or CP SIL 88 (1). However, in order to obtain infrared spectra with good signal/noise ratio, it was necessary to select a column with a high capacity (a few hundreds of ng per peak) and low bleeding level, but still having a good chromatographic resolution. For that reason, it was necessary to use a less polar phase. The chemically bonded Cp Wax 57 CB with a thick film (1.2 μm) appeared to be an excellent compromise for capacity over resolution.

The first step of the study was to obtain infrared spectra of 18:1Δ9 *cis* (Z) and of 18:1Δ9 *trans* (E) in order to detect the differences between *cis* (Z) and *trans* (E) isomers in the vapor phase. For that purpose, pure 18:1Δ9 *cis* (Z) and pure 18:1Δ9 *trans* (E)were injected in the GC-FTIR system. The resulting spectra showed significant differences in the finger print region (600–1000 cm^{-1}: out-of-plane δ CH) as well as in the CH stretching region around 3000 cm^{-1}. The *trans* (E) isomer is characterized by a medium absorption band at 968 cm^{-1} (970–960 cm^{-1} for the δ CH out-of-plane deformation in the condensed

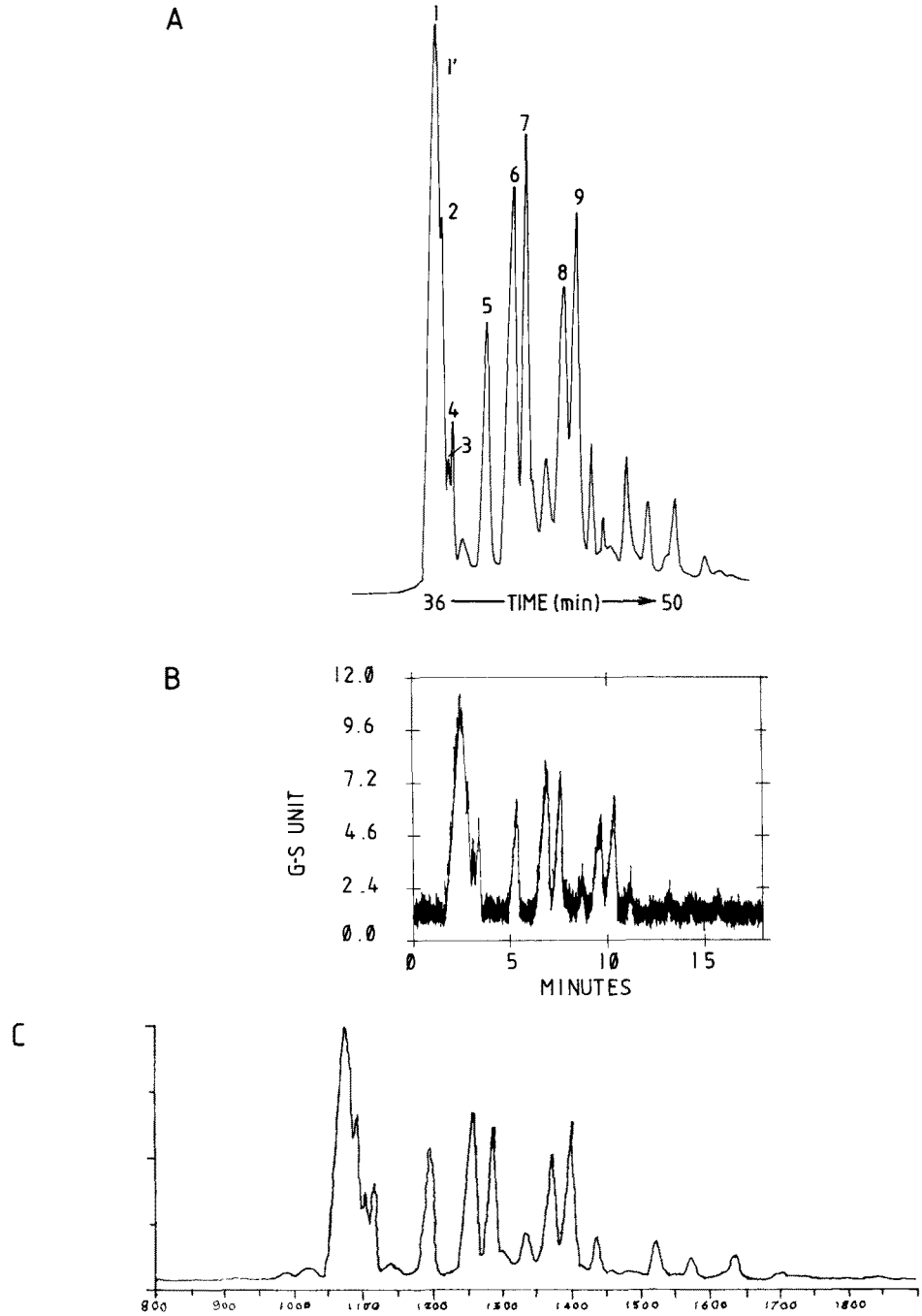


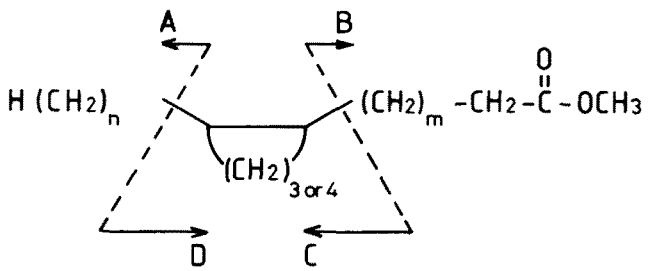
FIG. 1. A, GLC analysis of the CFAM fraction isolated from linseed oil heated at 275 C for 12 hr under nitrogen; B, the reconstructed IR chromatogram (Gram-Schmidt), and C, the total ion current chromatogram.

phase) and the *cis* (Z) isomer by weak to medium absorptions at 704 cm^{-1} (near 690 for δ CH in the condensed phase) and 3013 cm^{-1} (3040-3010 cm^{-1} for υCH in the condensed phase).

Infrared spectra of cyclohexene. The absorption bands of a *cis* (Z) ethylenic bond in a 6-carbon membered ring are quite different from those observed for ethylenic bonds on a straight carbon chain. The GC-FTIR spectrum of cyclohexene showed that this type of unsaturation was characterized by medium to strong absorptions at 660 cm^{-1} (compared to 704 cm^{-1} for an ethylenic bond on a straight chain fatty acid) and 3034 cm^{-1} for υC-H. Considering the difference in the finger print region (out-of-plane δ C-H), it will therefore be possible to distinguish between *cis* (Z) ethylenic bond in a 6-carbon membered ring or on a straight carbon chain.

Heated linseed oil. We have represented in Figure 1 the total GLC analysis of the CFAM fraction isolated from a heated linseed oil, the reconstructed IR chromatogram and the total ion current chromatogram. From the very complex CFAM mixture, it was possible to obtain the IR spectra as well as the mass spectra of nine peaks. All the nine MS analyses showed the presence of a molecular ion at m/e 292 (Table 1), which indicates that these CFAM isolated from a heated linseed oil are dienoic fatty acids.

Peaks 1,1′,3,4,6,7,8 and 9 showed the characteristic IR absorptions for *cis* (Z),*trans* (E) dienoic fatty acids while peaks 2 and 5 only show the IR absorption for a *cis* (Z),*cis* (Z) dienoic acid (Table 1). The δ C-H absorption for *cis* (Z) ethylenic bond ranged from 706 to 714 cm^{-1} for peaks 1,1′,2,3,4 and 5, while the δ C-H absorption for peaks 6,7,8 and 9 ranged from 658 to 662 cm^{-1}, corresponding to a shift of about 50 cm^{-1} (Fig. 2). Furthermore, the MS spectra of peaks 6,7,8 and 9 (Table 1, Fig. 2) show the presence of an ion at m/z 238 which corresponds to a retro Diels-Alder reaction. This fragment was not detected for peaks 1,1′,2,3,4 and 5. The GC-MS spectra obtained for peaks 6,7,8 and 9 were similar except for the relative intensity of the fragments m/z 55 to 81. All these data indicate that the peaks 6,7,8 and 9 are diunsaturated cyclic ester isomers with a cyclohexenyl ring.



The characteristic A-D fragmentations for cyclic esters (5,6,16) were observed (Fig. 2, m/z 43, 124, 168, 249). However, several intense fragmentations (m/z 238, 206 and 164) were characteristic of the cyclohexenyl ring. As previously outlined, the fragment at m/z 238 was due to a retro Diels Alder reaction. Loss of CH_3OH from m/z 238 gives a fragment at m/z 206, while a McLafferty rearrangement on m/z 238 would explain the m/z 164 fragment. The MS spectra for peaks 6,7,8 and 9 are similar to those published by Awl and Frankel for the 9-(6-propyl-3-cyclohexenyl)-8 nonenoate (17). A very good match existed for the MS of 6 and 7. This was also the case for peaks 8 and 9. The difference observed between these two groups (6,7 and 8,9) was in the relative intensity of the m/z 55-81 fragments. This could indicate that the two peaks 6 and 7 and the two peaks 8 and 9 are *cis/trans* isomers (ring substitution), whereas the two groups differ by the position of the *trans* (E) ethylenic bond on the carbon chain. The total structure of these components will be studied using TMS derivatives in order to localize the ethylenic bond on the carbon chain as usually described for the straight chain fatty acids (18-20).

TABLE 1

Molecular Weight and IR Data for CFAM Isolated From a Linseed Oil Heated at 275 C for 12 hr Under Nitrogen

Peak no. (Fig. 1)	MS (m/z)	IR (cm^{-1})	
		cis (Z)	*trans* (E)
1	292	(712)	(966)
1′	292	(712)	(966)
2	292	(719)	
3	292	(714)	(966)
4	292	(712)	(972)
5	292	(706)	
6	292 (238)	(660)	(970)
7	292 (238)	(658)	(968)
8	292 (238)	(662)	(968)
9	292 (238)	(660)	(968)

Different GC-MS spectra were obtained for peaks 1,1′,2,3 and 5, as illustrated in Figure 3. In every case, the peak of m/z 80 was the base peak. A close examination of the mass spectra and the IR spectra does not permit to propose a structure directly for these components. However, their retention times compared with those of the hydrogenated fraction (2) seem to indicate that these components could be some 5 carbon membered ring isomers. In 1956 and 1961, McDonald and McInnes described the IR spectra in condensed phase of a non urea adduct fraction isolated from a heated linseed oil (21,22). The IR absorption at 660 cm^{-1} which was already observed was attributed to the possible presence of an ethylenic bond in a six-membered ring. The present results seem to confirm this observation. However, according to McDonald and McInnes, the absence of an absorption at 660 cm^{-1} does not necessarily indicate the absence of a cyclohexene ring. For example, a second ethylenic bond attached directly to the ring could hinder the C-H out-of-plane deformation of the ring ethylenic bond. It will therefore be necessary to use the TMS derivatives and/or ozonolysis to study the complete structures of the cyclic fatty acids 1,1′,2,3,4 and 5.

Heated sunflower oils. The GC-MS analyses (Tables 2 and 3) indicated that all the cyclic monomers isolated from a sunflower oil heated under nitrogen (Fig. 4) and those isolated from an oil heated under air (fraction 3, Fig. 5) had a molecular weight of 294. This indicates that

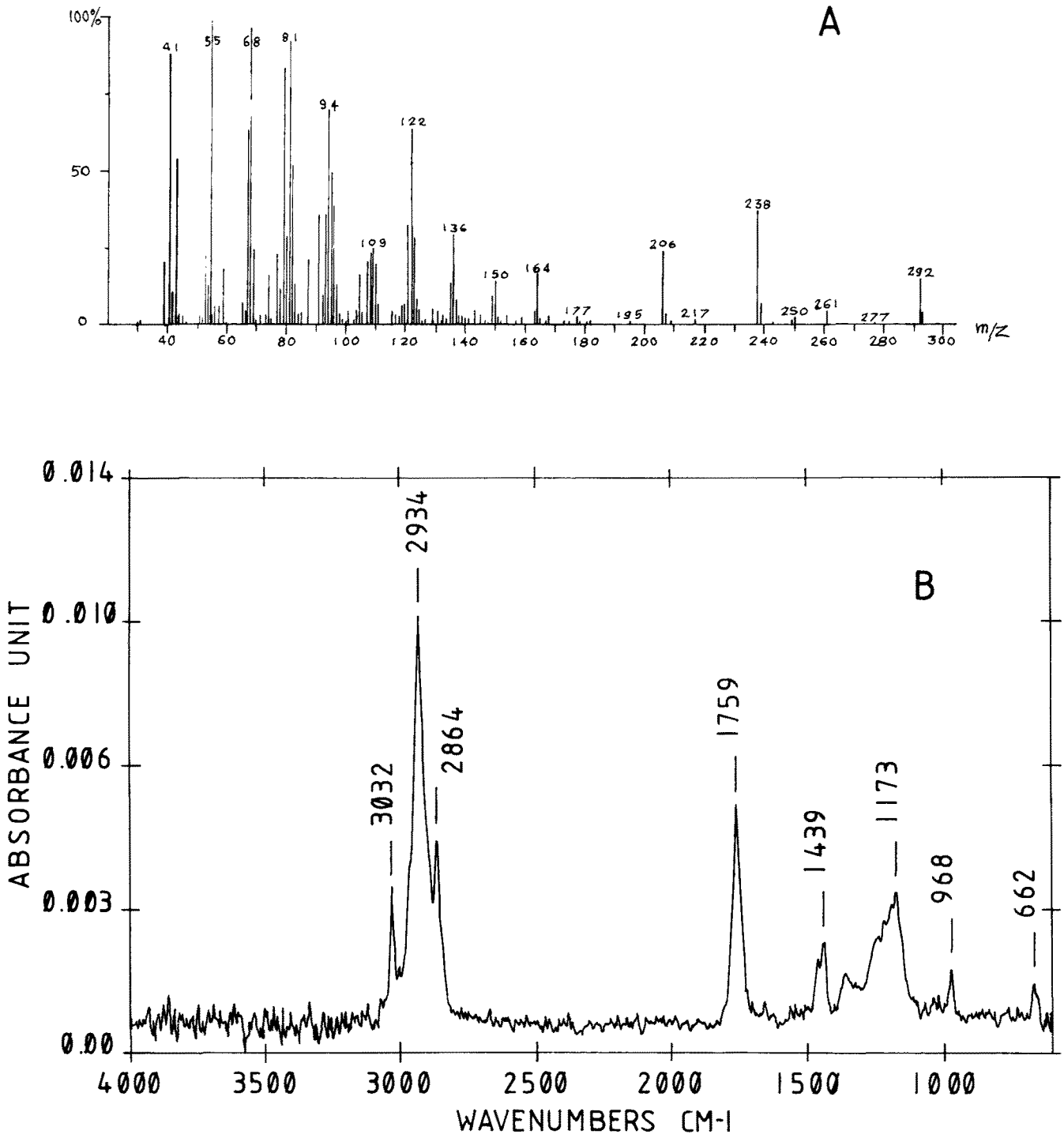


FIG. 2. GC-MS, A, and GC-FTIR spectra, B, of peak no. 8 (Fig. 1) of a mixture of CFAM isolated from linseed oil heated at 275 C for 12 hr under nitrogen.

these CFAM are monounsaturated fatty acids. However, fraction 4 isolated from a sunflower oil heated under air (Fig. 6) contained some saturated fatty acids as shown in a previous paper (1). Peaks 2-4, 3-4, 5-4, 6-4 and 7-4 had a molecular weight of 296, while peaks 8-4 and 15-4 had a molecular weight of 294. This could indicate that peaks 8 to 15 are bicyclic components. The IR absorptions (Tables 2 and 3) showed the presence of *cis* (Z) and *trans* (E) ethylenic bonds in both the sunflower oil heated under nitrogen and the sample heated in the presence of air. The CFAM having a *cis* (Z) ethylenic bond seem to have, in general, shorter retention time than those with

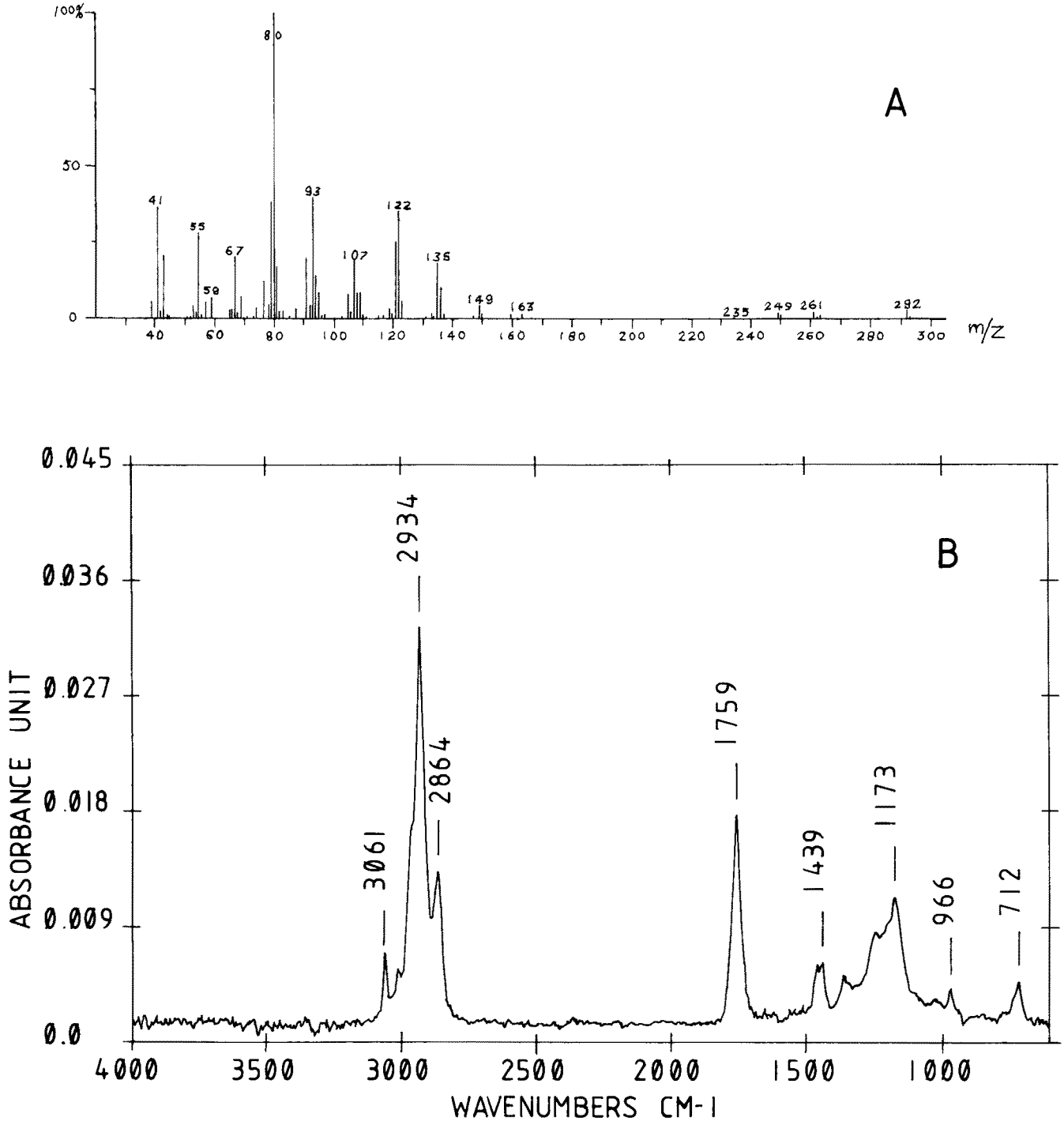


FIG. 3. GC-MS, A, and GC-FTIR spectra, B, of peak no. 1 (Fig. 1) of a mixture of CFAM isolated from a linseed oil heated at 275 C for 12 hr under nitrogen.

a *trans* (E) ethylenic bond (Tables 2 and 3). It was impossible to determine the geometry of the ethylenic bond in peaks 7T, 9T and 10T, as these components did not give clean spectra.

We have reported in Table 4 the MS fragmentations of some CFAM for which we could directly propose a structure. However, it will be necessary to synthesize some TMS derivatives to study the structures of the other CFAM of Figures 4, 5 and 6 as well as to give the position of the ethylenic bond for some components reported in Table 4. The fragmentations indicate that peaks 1T and 3T were isomers. This is also the case for the pairs 2T and 4T, 1-3 and 2-3, 3-3 and 4-3 and 6-4, 7-4. Furthermore, the pairs 1-3, 2-3 and 3-3, 4-3 seem to be isomers of 1T and 2T, respectively. The peak 8-3 also seems to be an isomer of peak 4T. The proposed

structures for the components reported in Table 4 are represented in Figure 7. However, great care must be taken in the interpretation of the spectra of components 1-3, 2-3, 3-3 and 4-3. The components 1-3 and 2-3 are not well separated even on a polar column (1). This is also the case for components 3-3 and 4-3. The GLC analysis (Fig. 5) seems to indicate the presence of two components which could only differ by the position of the ethylenic bond in the ring in each of the first two peaks, but it could be possible that the MS spectra obtained are not characteristic of the pure components. It would therefore be interesting to try to fractionate these two pairs in order to confirm the structures proposed for these four CFAM (Fig. 7).

A simple fragmentation was obtained for the CFAM with a 6-carbon membered ring (Table 4, peaks 6-4 and 7-4). The different fragments observed (A,B,C and D) corresponded to a fragmentation in the α position as previously described (5,6,16). In that case, the fragment B + 1 was always more intense than the fragment B. The fragmentation of the other components described in Table 4 was not as simple. In each case, two series D,D-32, D-32-18 were observed. For example, the fragmentation of component 1T (Fig. 8) gave the series 209, 177, 159 and 223, 191, 173. However, the intensity of the fragments 223, 191 and 173 was much lower if compared with those of fragments 209, 177 and 159. A possible explanation is the existence of both an α and a β cleavage for those CFAM presenting the two series D, D-32 and D-32-18. In that case, the α fragmentation is always more likely to occur if compared with the β one. For component 1T an α fragmentation would give the ions 209, 177 and 159 while a β fragmentation would give the ions 223, 191 and 173. The alkyl substituent would therefore be a hexyl chain (fragment A m/z = 85). Moreover, fragments B (m/z = 143) and C (m/z = 151) suggest a cyclopentene ring, leading to the structure proposed in Figure 7. The other structures in Figure 7 are proposed from the same reasoning. These cyclopentenic derivatives already have been suggested (3,7,22,23), and a β cleavage has been observed in cyclopentene derivatives (24). For compound 1T, this β cleavage on the ester chain would account for the minor ions 129 and 165 (Fig. 8). It is also interesting to note that the fragment B+1 of the cyclopentane derivatives cannot always be detected. All the components described in Table 4, except 2-4, 5-4, 6-4 and 7-4 seem to have an ethylenic bond in a 5-carbon membered ring. However, it is somewhat surprising to observe no difference in the characteristic IR absorption for the *cis* (Z) ethylenic bond (Fig. 8, Table 2) if compared with an ethylenic bond on a straight carbon chain (Table 1). The TMS derivatives of these CFAM will be studied in order to confirm these structures, to determine the exact position of the ethylenic bond, and to study the other CFAM.

Linseed oil is rich in linolenic acid and sunflower oil in linoleic acid (1). These results indicate that the heat treatment of linolenic acid under the conditions described in the experimental part give mainly some *cis* (Z),*trans* (E) diethylenic CFAM while the heat treatment of linoleic acid give a mixture of *cis* (Z) and *trans* (E) monoethylenic CFAM isomers. We have detected the presence of both cyclohexanic and cyclopentanic CFAM. The next step of

TABLE 2

Molecular Weight and IR Data for CFAM Isolated from a Sunflower Oil Heated at 275 C for 12 hr Under Nitrogen

Peak no. (Fig. 4)	MS (m/z)	IR (cm^{-1})
1T	294	*cis* (Z) (712)
2T	294	*cis* (Z) (712)
3T	294	*cis* (Z) (712)
4T	294	*cis* (Z) (710)
5T	294	*trans* (E) (966)
6T	294	*trans* (E) (972)
7T	294	—
8T	294	*trans* (E) (972)
9T	294	—
10T	294	—

TABLE 3

Molecular Weight and IR Data for CFAM (Fraction 3) Isolated From a Sunflower Oil Heated at 200 C for 48 hr in Air

Peak no. (Fig. 5)	MS (m/z)	IR (cm^{-1})
1-3	294	*cis* (Z) (714)
2-3	294	*cis* (Z) (712)
3-3	294	*cis* (Z) (714)
4-3	294	*cis* (Z) (714)
5-3	294	*cis* (Z) (714)
6-3	294	*cis* (Z) (714)
7-3	294	*trans* (E) (968)
8-3	294	*cis* (Z) (716)
9-3	294	*trans* (E) (968)
10-3	294	*trans* (E) (968)
11-3	294	*trans* (E) (968)

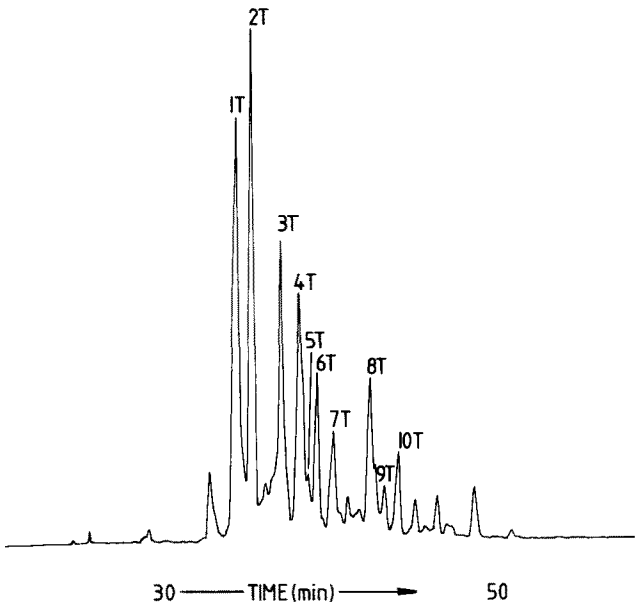


FIG. 4. GLC analysis on a CpWax 57 CB of a mixture of CFAM isolated from a sunflower oil heated at 275 C for 12 hr under nitrogen.

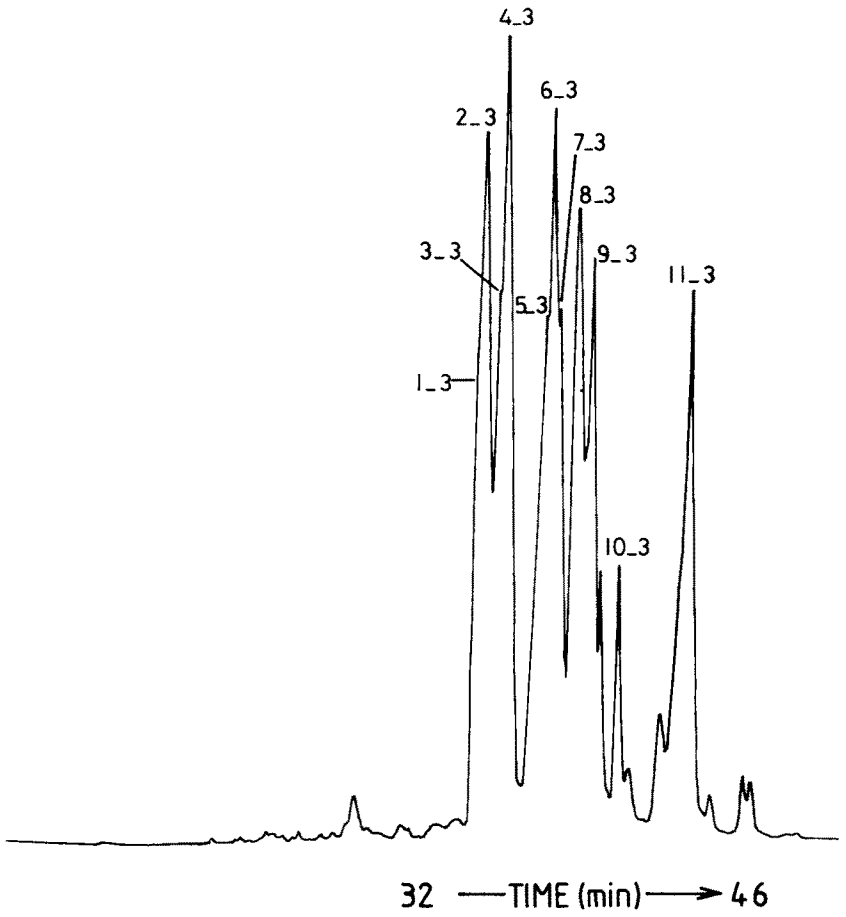


FIG. 5. GLC analysis on CpWax 57 CB of a mixture of CFAM (Fraction 3) isolated from a sunflower oil heated at 200 C for 48 hr.

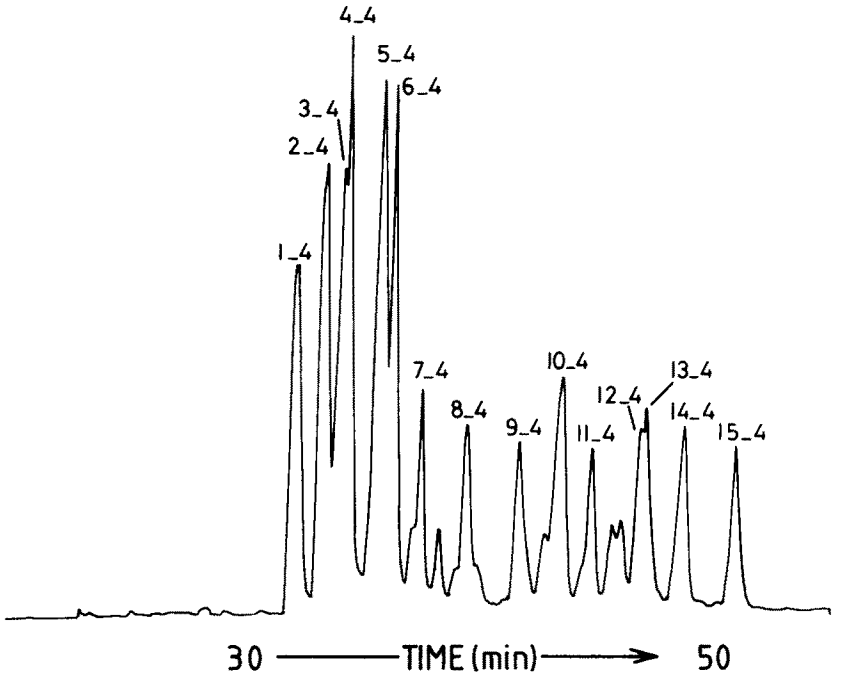


FIG. 6. GLC analysis on a CpWax 57 CB of a mixture of CFAM (Fraction 4) isolated from a sunflower oil heated at 200 C for 48 hr.

TABLE 4

GC-MS Fragmentations of Some Cyclic Fatty Acid Monomers Isolated From Heated Sunflower Oils[a]

Compound	Ion fragment : m/z (% relative intensity)									
	M+	M-31	D	D-32	D-32-18	B+1	B	C	A	Base
1T (Fig. 4)	294 (10)	263 (5)	209 (6) 223 (2)	177 (10) 191 (1)	159 (8) 173 (0.5)	144 (0.5)	143 (3)	151 (15)	85 (3)	67 (100)
2T (Fig. 4)	294 (12)	263 (7)	237 (5) 251 (1)	205 (7) 219 (0.5)	187 (12) —	—	171 (2)	123 (55)	57 (3)	67 (100)
3T (Fig. 4)	294 (10)	263 (4)	209 (6) 223 (1)	177 (12) 191 (2)	159 (10) 173 (1)	144 (1)	143 (4)	151 (15)	85 (2)	67 (100)
4T (Fig. 4)	294 (11)	263 (6)	237 (4) 251 (1)	205 (5) —	187 (10) 201 (0.5)	—	171 (1)	123 (52)	57 (5)	67 (100)
1-3 (Fig. 5)	294 (8)	263 (4)	209 (5) 223 (1)	177 (9) 191 (1)	159 (7) 173 (1)	—	143 (2)	151 (14)	85 (3)	67 (100)
2-3 (Fig. 5)	294 (8)	263 (3)	209 (4) 223 (1)	177 (8) 191 (2)	159 (7) 173 (1)	—	143 (2)	151 (14)	85 (3)	67 (100)
3-3 (Fig. 5)	294 (8)	263 (8)	237 (5) 251 (1)	205 (6)	187 (15) 201 (1)	172 (0.5)	171 (2)	123 (84)	57 (6)	67 (100)
4-3 (Fig. 5)	294 (8)	263 (5)	237 (3) 251 (1)	205 (4) 219 (0.5)	187 (8) 201 (0.5)	—	171 (2)	123 (51)	57 (5)	67 (100)
6-3 (Fig. 5)	294 (8)	263 (3)	209 (4) 223 (1)	177 (8) 191 (2)	159 (7) 173 (1)	144 (0.5)	143 (2)	151 (13)	85 (3)	67 (100)
8-3 (Fig. 5)	294 (5)	263 (5)	237 (2) 251 (0.5)	205 (3) 219 (0.5)	187 (7) 201 (0.5)	—	171 (1.5)	123 (44)	57 (6)	67 (100)
2-4 (Fig. 6)	296 (3)	265 (2)	239 (2) 253 (3)	207 (5) 221 (1)	189 (6) 203 (1)	172 (3)	171 (2)	125 (16)	57 (25)	55 (100)
5-4 (Fig. 6)	296 (3)	265 (2)	239 (2) 253 (2)	207 (5) 221 (1)	189 (6) 203 (1)	172 (2)	171 (2)	125 (15)	57 (23)	55 (100)
6-4 (Fig. 6)	296 (5)	265 (2)	253 (11)	221 (10)	203 (7)	172 (13)	171 (2)	125 (37)	43 (40)	69 (100)
7-4 (Fig. 6)	296 (2)	265 (1)	253 (9)	221 (8)	203 (6)	172 (11)	171 (1)	125 (40)	43 (42)	69 (100)

[a]Figs. 4-6.

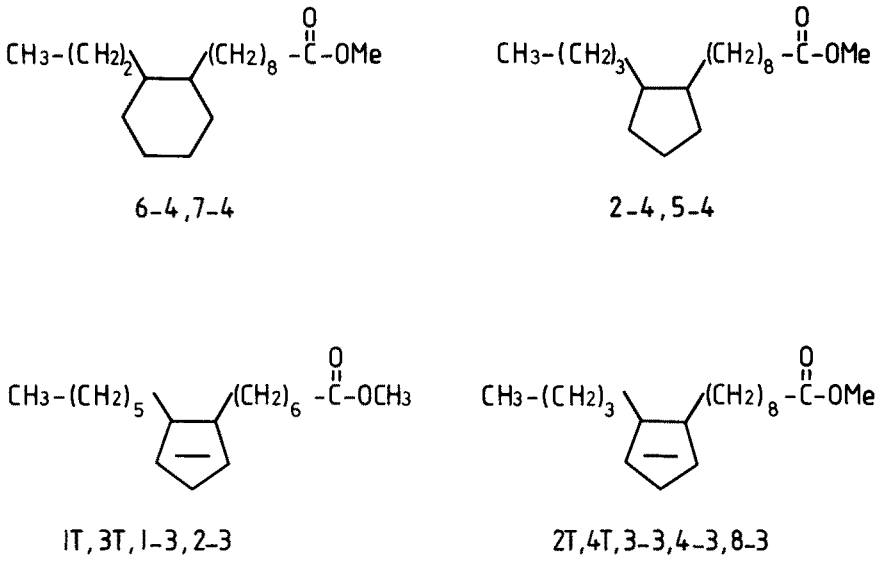


FIG. 7. Proposed structures for some CFAM isolated from sunflower oils heated at 275 C under N_2 and at 200 C under air.

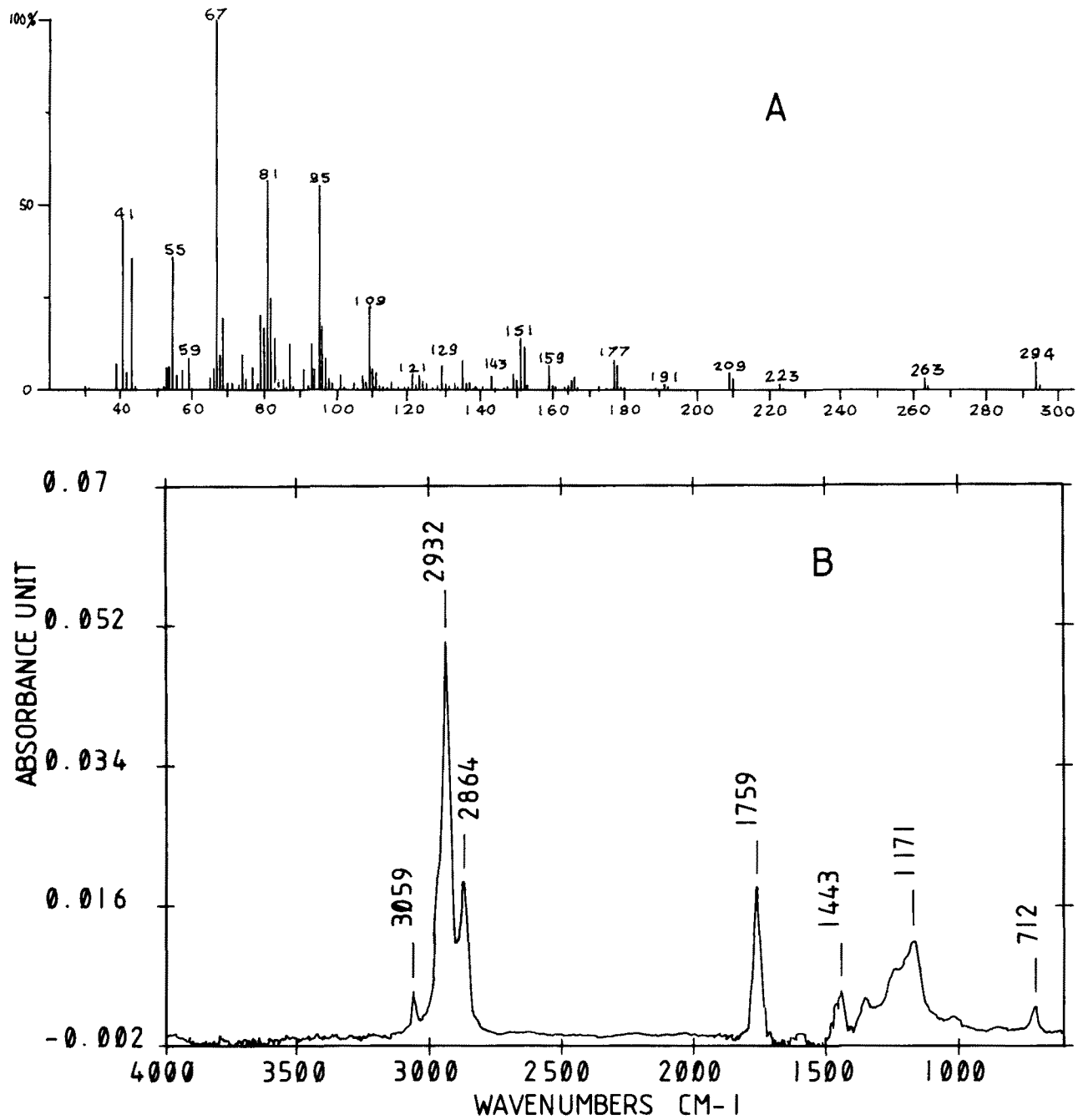


FIG. 8. GC-MS, A, and GC-FTIR, B, spectra of peak no. 1T (Fig. 4) of a mixture of CFAM isolated from a sunflower oil heated at 275 C for 12 hr under nitrogen.

our ongoing study will be to synthesize the TMS derivatives in order to report the complete structure of the molecules.

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[Received September 15, 1986]