Mass Spectrometry of Lipids. II. Monoglycerides, Their Diacetyl Derivatives[1] and Their Trimethylsilyl Ethers

Cecil B. Johnson[2] and **Ralph T. Holman**, The Hormel Institute, University of Minnesota, Austin, Minnesota

ABSTRACT

The mass spectra of 1- and 2-monoglycerides, their diacetyl derivatives and their trimethylsilyl (TMS) ether derivatives were recorded at high (80 eV) and low (6–13 eV) voltages. The fatty acid components of these derivatives included the even-numbered saturated acids from capric to arachidic acid plus oleic, linoleic and linolenic acids. Differences between isomeric 1- and 2-monoglycerides were not sufficient to provide a basis for the analysis of these isomers. Mass spectra of the monoglycerides were very similar to the corresponding methyl esters. Mass spectra of the diacetyl derivatives were qualitatively similar to triglycerides of long-chain fatty acids, but parent ions were not observed. The spectra of diacetyl derivatives may be used for distinguishing 1- and 2-monoglycerides, but the spectra of the TMS ethers are better in this regard. The latter derivatives have fragmentation patterns distinct for the 1- and 2-monoglyceride isomers, particularly at low electron voltages.

INTRODUCTION

MASS SPECTRA of a wide range of saturated and unsaturated fatty acids and esters, both substituted and unsubstituted, have been investigated (1–4). With less volatile compounds, such as glycerides, difficulties associated with decomposition of the sample (5) and pumping out of the sample from the spectrometer are experienced when a conventional inlet system is used (3). This problem has been overcome by the development of a direct injection inlet in which the sample is placed at the entrance to the ion source. With this system mass spectra of triglycerides up to tribehenin have been reported (6,7). The fatty acids in the one and three positions of the triglyceride molecules could be identified by the presence of corresponding acyloxymethylene peaks in the spectra (3,6). Thus, 1- and 2-oleo-distearin could be readily distinguished by these peaks (6). A similar distinction might be made between 1- and 2-monoglycerides on either the parent compounds or their derivatives. If so, gas chromatography of volatile derivatives such as the diacetyl and the trimethylsilyl ethers of monoglycerides might be combined with mass spectrometry for the separation and identification of monoglycerides (8–10).

Thus far, the mass spectra of monoglycerides and their derivatives have not been reported. It seemed likely that mass spectra might be useful for characterization of the structures of these compounds. Therefore, 1- and 2-monoglycerides were prepared from straight-chain saturated fatty acids of even carbon number from capric acid to arachidic acid, and from the unsaturated acids, oleic, linoleic and linolenic acids. Diacetyl derivatives and trimethylsilyl (TMS) ethers of the monoglycerides were also prepared. The mass spectra were recorded with use of a direct inlet system in which pyrolysis is minimized.

EXPERIMENTAL

Fatty acids of purity >99% were obtained from The Hormel Institute, Austin, Minnesota. 1-Monoglycerides were prepared by acylation of *dl*-1,2-isopropylidene glycerol with fatty acid chlorides (11), followed by removal of the isopropylidene group (12). 2-Monoglycerides were prepared in a similar manner via 1,3-benzylidene glycerol (11). They were purified either by crystallization from diethyl ether-hexane or by thin-layer chromatography on borate-impregnated silica gel (13) with chloroform:acetone (75:25) as the solvent. The borate complexes were eluted from the plates with diethyl ether, these were decomposed by washing the solution with distilled water, and the monoglycerides were recovered. The purity of the monoglycerides was checked by TLC on borate-impregnated plates or by GLC of the TMS derivatives (9).

Diacetyl derivatives were prepared by acylation of the monoglycerides with acetyl chloride in pyridine (11). Reaction of the monoglycerides with hexamethyldisilazane in the presence of trimethylchlorosilane and pyridine was used for the preparation of the trimethylsilyl ether derivatives (9).

[1] For the first paper in this series, see reference 1.

[2] Permanent address: Fats Research Division, D.S.I.R., P. O. Box 8021, Wellington, New Zealand.

A mass spectrometer (Hitachi-Perkin Elmer Model RMU-6D) equipped with a direct evaporation system (MG-150) was employed. The sample in a small cup on the tip of a rod was inserted through a vacuum lock into a heating block just outside the ionization chamber. The sample evaporated from the cup directly into the ion source at about 70C, and a spectrum was recorded when the evaporation, as measured by a total-ion monitor, settled to a constant rate. Sample pressure was in the order of 5×10^{-7} torr, measured in the source housing.

Thermal decomposition of the monoglycerides in this system was minimized as evidenced by the small M-18 peak (loss of water) in the spectra. Mass spectra were obtained at both high (80 eV) and low electron voltages. The higher electron voltage spectra were more reproducible, though more complex, than those recorded at the low voltages. In the latter case the actual voltage was the lowest that produced a countable spectrum, and this was usually between 6 and 13 eV. Peaks of high mass were more prominent in the low voltage spectra, whereas extensive breakdown of the molecules to short hydrocarbon and oxygen-containing chains was observed in spectra at the high voltage.

RESULTS AND DISCUSSION

Monoglycerides

The mass spectra of 1- and 2-monomyristin are shown in Figure 1, and a summary of significant peaks is given in Table I. The spectra can be divided into hydrocarbon and oxygen-containing peaks, the latter being more prominent in the low electron voltage spectra. Significant differences exist between the spectra of the saturated and unsaturated monoglycerides. Within each of these series, the intensities of many of the peaks changed progressively according to the chain length or the degree of unsaturation of the fatty acid. Differences between the spectra of 1- and 2-monoglycerides were not sufficiently large or consistent to provide a basis for the analysis of these isomers. A series of peaks was observed corresponding to ions of structure

$$-CH{=}CH-CH_2-O-CO(CH_2)_n$$

for 1-monoglycerides or

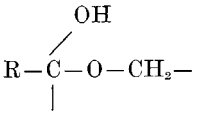
$$CH_2{=}C(CH_3-)-O-CO-(CH_2)_n$$

for 2-monoglycerides where

$n = 0$ to 9. These structures were assigned on the basis of similar peaks in the spectra of methyl esters (14).

Saturated Monoglycerides

Spectra at High Electron Voltage. Peaks corresponding in mass to fatty acid and methyl ester were present in the spectra of monoglycerides. These ions were probably formed by fragmentation of the glycerol moiety with prior migration of a hydrogen atom, to give in the latter instance a probable transient structure of



The peak corresponding to the fatty acid ion plus one was of greater intensity than that expected from isotope ratios, and is probably formed by an acyloxy-fragmentation with a rearrangement involving two hydrogen atoms (2). In the spectra of monoglycerides containing the shorter chain fatty acids, the peak for fatty acid + 1 was more intense than the acid ion peak. This phenomenon was also observed in the mass spectra studied of short-chain ethyl esters and long-chain esters of propyl and higher alcohols and formates but not of long-chain methyl or ethyl esters (2,4,14,15).

Increasing the chain length of the fatty acid resulted in an increase in the intensity of the acid ion peak, whereas the intensity of the acylium ion decreased. The latter change paralleled a decrease in the P-31 peak which signifies the loss of hydroxymethylene group ($-CH_2OH$) from the parent ion, P. A metastable peak corresponding to the transition [P-31] $\longrightarrow$ $CH_3(CH_2)_nCO-$ was prominent in each spectrum, indicating that the acylium ion was derived to some extent from the P-31 ion.

In each of these spectra, the base peak was due to a three-carbon fragment (C_3H_7- m/e = 43) which, however, was absent or of very low intensity at the low voltages. This fragment was third in prominence, behind those corresponding to $CH_3-O-C(OH){=}CH_2$ and $CH_3-O-CO-CH_2-CH_2-$, in the mass spectra of the corresponding methyl esters (14).

Spectra at Low Electron Voltage. Peaks in the high mass regions were of slightly greater intensities than in the corresponding high voltage spectra. Main differences arose in the low and medium mass ranges of the spectra, and a change in the base peak from one corresponding to a hydrocarbon fragment to one of an oxygen-containing ion. The base peak of a monoglyceride containing a short-chain fatty acid was the acylium ion. This peak decreased in intensity with increasing chain

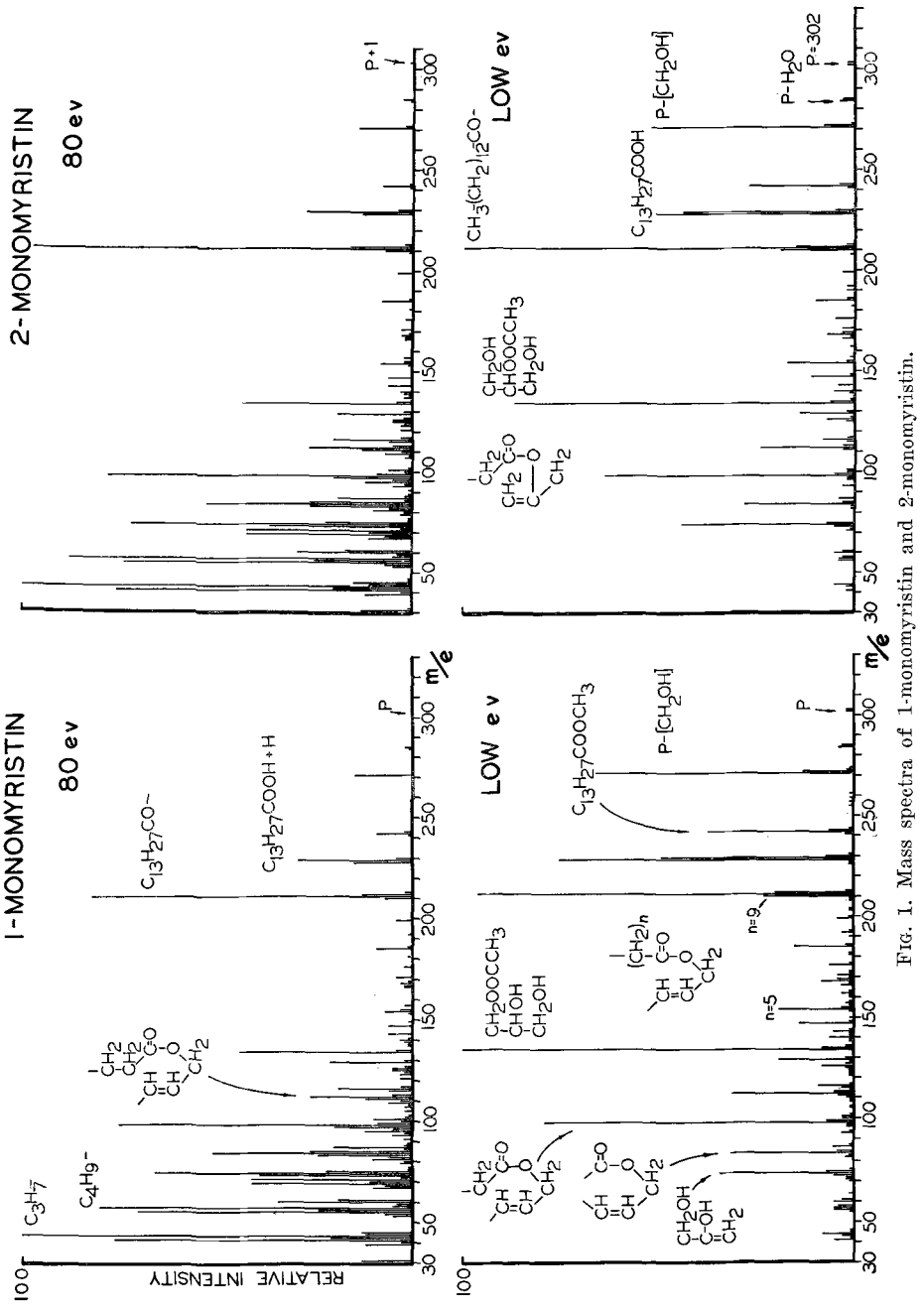


FIG. 1. Mass spectra of 1-monomyristin and 2-monomyristin.

length of the fatty acid, whereas that for the acid ion increased to become the base peak. Peaks due to hydrocarbons were not measurable in most cases.

In some instances, especially in the spectra of monoglycerides containing short-chain fatty acids, the peak of the rearranged monoacetin ion (m/e = 134) became prominent, analogous to the rearranged methyl acetate ion peak at m/e = 74 in spectra of methyl esters (14), and was of an intensity equal to or slightly greater than the acylium peak. It is evident that the glycerol part of the ion is susceptible to the loss of water or a hydroxy-methylene group to produce peaks of m/e = 116 or m/e = 103, respectively. These losses take place either

TABLE I

Monoglyceride Mass Spectra

Fatty acid ion	MG[a]	10:0		12:0		14:0		16:0		18:0		20:0		18:1		18:2		18:3	
		H.V.[b]	L.V.[c]	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.
Parent ion (P)	1	....	....	0.8	1.1	....	1.9	....	8.5	0.7	1.2	1.0	8.3	1.5	18	2.7	32	2.4	100
" "	2	0.7	....	0.9	1.5	....	1.5	0.8	1.0	1.2	7.7	0.7	8.5	1.2	10.2	1.4	34	15	100
P—[OH]	1	....	....	2.1	1.7	2.2	2.6	1.2	5.4	1.6	2.5	1.3	11	....	....	1.0	2.8	0.5	0.7
" "	2	1.3	4.1	2.6	2.6	3.2	2.9	....	5.0	0.9	3.1	0.7	....	....	....	0.6	2.5	0.5	0.8
P—[H_2O]	1	....	....	0.6	1.3	1.0	3.9	1.0	11	1.4	3.7	0.9	16	1.2	2.9	1.9	9.3	....	0.7
" "	2	....	7.1	0.9	3.7	14	3.5	1.8	....	1.5	9.2	1.2	6.6	3.4	3.7	1.1	8.6	0.7	3.0
P—[CH_2OH]	1	7.6	....	15	44	15	66	5.5	65	7.2	19	3.2	52	1.9	8.1	0.6	....	1.4	0.5
" "	2	9.3	62	20	94	14	52	4.0	42	7.5	44	4.5	15	2.9	7.9	...	....	4.8	0.9
Acyl $CH_3(CH_2)_nCO$	1	62	45	93	100	82	96	31	68	40	28	16	53	20	20	29	22	3.9	10
" "	2	94	100	98	100	96	100	37	92	43	46	22	19	29	24	21	21	14	8.4
$CH_2(CH_2)_nCO$	1	1.1	5.9	4.6	12	6.6	23	4.3	32	9.1	15	4.8	45	39	100	55	100	2.6	0.5
" "	2	4.4	20	6.6	27	7.0	19	4.1	26	10	30	7.2	14	51	100	39	100	5.5	....
Acid $CH_3(CH_2)_nCOOH$	1	7.7	19	8.2	25	15	75	11	100	51	100	12	100	1.4	15	8.8	41	0.9	4.0
" "	2	3.4	37	10	46	13	51	4.2	39	25	100	27	100	1.4	6.0	3.3	25	3.4	11
Acid + H	1	18	14	30	44	29	49	10	41	21	27	6.8	40	0.5	4.4	2.2	10	1.1	1.9
" "	2	18	44	29	47	27	44	9.0	29	16	32	11	25	0.6	1.8	0.7	5.1	2.0	3.5
Methyl ester	1	2.9	....	8.8	25	8.9	37	3.8	34	5.4	11	2.3	28	....	....	....	1.6	....	1.0
" "	2	4.0	29	10	40	7.5	27	2.8	23	5.3	22	3.4	8.0	....	0.9	....	....	....	....
Monoacetin	1	12	14	36	78	44	100	21	94	31	21	20	80	3.8	....	3.6	....	6.5	3.1
"	2	21	60	40	100	43	87	30	100	35	56	25	4.7	5.8	1.6	3.5	0.7	7.8	....
C_3H_7	1	100	23	100	1.1	100	2.5	100	3.1	100	1.1	100	1.4	56	....	29	....	67	....
"	2	100	12	100	....	100	1.7	100	6.0	100	....	100	2.0	66	....	36	....	33	....
$-CH_2CH_2CH=CH_2$	1	70	22	72	0.5	70	0.8	62	6.8	83	....	62	0.5	100	....	73	....	10	....
" "	2	55	4.7	66	3.1	73	....	69	....	71	....	69	6.8	100	....	78	....	82	....
$-CH_2CH=CHCH=CH_2$	1	9.0	4.6	9.1	....	10	....	8.0	....	15	....	8.6	....	4.3	....	100	....	79	....
" "	2	6.7	2.9	8.0	....	11	....	12	....	12	....	11	3.2	65	....	100	....	86	....
$-CH=CH-CH=CH-CH=CH_2$	1	2.7	3.2	2.3	....	2.9	....	1.8	...	4.6	....	1.8	....	8.4	....	42	....	100	....
" "	2	2.1	....	2.0	....	2.7	....	3.2	....	3.2	....	2.6	....	21	....	42	....	100	....
m/e = 98	1	30	100	82	4.6	75	79	44	75	71	14	48	54	46	....	9.5	....	21	0.7
" "	2	26	85	52	45	77	64	71	74	71	34	62	6.2	49	5.1	7.8	....	12	....

[a] MG = monoglyceride.
[b] H.V. = high electron voltage.
[c] L.V. = low electron voltage.

from the parent ion or after the loss of the hydrocarbon fragment from the parent ion.

Unsaturated Monoglycerides

Spectra at High Electron Voltage. The base peaks of these spectra were the unsaturated hydrocarbon fragments of m/e 55 for oleate ($\cdot CH_2-CH_2-CH=CH_2$), 67 for linoleate ($\cdot CH_2-CH=CH-CH=CH_2$) and 79 for linolenate ($\cdot CH=CH-CH=CH-CH=CH_2$). These were the major hydrocarbon peaks observed in the spectra of the corresponding fatty acid methyl esters (16). Compared with the spectra of 1- and 2-monostearins, significant decreases in the intensities of the peaks corresponding to the methyl ester, acid ion and acid-plus-one ion were observed, with a smaller decrease in intensity of the acylium ion. The intensities of the peaks in the high mass regions of these spectra were similar to those of corresponding peaks of the monostearins. However, a metastable peak for the transition [P-31] ⟶ acylium ion was not observed.

Spectra at Low Electron Voltage. A large increase in intensity of the parent ion peak was observed with increase in unsaturation of the fatty acid component, and this peak was the base peak in the spectra of the monolinolenins. Such parent ion peaks have been observed in the spectra of the corresponding methyl esters (16). Peaks corresponding to the loss of a hydroxyl group or water from the parent ion were of similar intensity to the corresponding peaks in spectra of the monostearins, but the intensity of the peak caused by the loss of a hydroxymethylene group was much less. The intensities of the methyl ester ion, acid ion, acid-plus-one ion and monoacetin ion peaks showed similar patterns, and this is probably a reflection of the greater stability of the parent ions.

The base peaks in the monoolein and monolinolein spectra were those corresponding to the acylium fragment minus one, i.e., the loss of glycerol from the parent ion rather than the glyceryl group, as is the case for saturated monoglycerides. In the mass spectrum of methyl oleate (16), the base peak corresponded to the loss of methanol from the parent ion (P-32), whereas this peak was insignificant in the spectrum of methyl linolenate where the P-31 peak (loss of methoxy group) becomes the more prominent of the two. Thus, the unsaturated monoglycerides and the corresponding methyl esters have similar fragmentation patterns.

Diacetyl Derivatives of the Saturated Monoglycerides

Spectra at High Electron Voltage. The high voltage spectra of 1,2-diacetyl-3-myristin and 1,3-diacetyl-2-myristin are shown in Figure 2. Intensities of peaks relevant to this study are shown in Table II. Because the diacetyl derivatives are triglycerides, similarities in the spectra of diacetins and other triglycerides should be apparent. Parent ion peaks were not observed in these spectra, as was the case for triacetin and other mono-acid triglycerides studied in this and other laboratories (3,17). Triglycerides having three different long-chain fatty acid moieties have been reported to yield parent ion peaks in their spectra (6,7), the intensity of which probably depends on the sample insertion system and instrument used.

Unlike the triglycerides containing only long-chain fatty acids, the base peaks of spectra of the diacetins corresponded to fragments of m/e = 43 as was the case with the monoglycerides. Because this peak was very small or nonexistent in the low voltage spectra, it is probably a hydrocarbon radical arising by secondary fragmentation of the long-chain acid moiety. As in other triglyceride spectra, loss of the long-chain acyloxy groups to produce a charged residue of m/e = 159 was, in general, the second most intense peak, especially with the 2-monoglyceride derivatives. The acyl ions and ions resulting from the loss of methylene acetate (CH_3COOCH_2-) from the parent ions were also prominent. The loss of the long-chain acyloxymethylene groups was more prominent in the derivatives of the 1-monoglycerides. These differences, though too small for the analysis of monoglyceride mixtures, can be used for distinguishing between isomers. In general, the intensity of these peaks increased with increase of the chain length of the fatty acid. An ion, formed by the loss of the long-chain fatty acid was also prominent in both groups of spectra. Loss of the acetyloxy group, acetic acid or methylene acetate, in most instances, resulted in small peaks in the spectra.

Spectra at Low Electron Voltage. No generality may be stated regarding the position of the base peak in these spectra. However, peaks corresponding to fragmentations described immediately above provided similar patterns, and the differences between the spectra of isomeric saturated monoglyceride derivatives were similar to those described above for spectra at high electron voltage. Peaks due to the loss of the acetyloxy group were more intense in these than in the high electron voltage spec-

tra, especially for monoglycerides containing long-chain fatty acid moieties.

Diacetyl Derivatives of the Unsaturated Monoglycerides

Spectra at High Electron Voltage. The base peak in all cases was the hydrocarbon fragment of m/e = 43 which was absent in the low voltage spectra. Other than short-chain fragments of m/e <200, there were few peaks of significance. Those present showed a pattern similar to the corresponding peaks in the spectra of the monostearin derivatives.

Spectra at Low Electron Voltage. In all cases, the m/e = 159 peak indicating loss of the long-chain acyloxy group from the parent ions was prominent. The base peaks for the 2-monoolein and 2-monolinolenin derivatives were the acyl ion minus one and the acyl ion, respectively. Other peaks in the spectra were, in general, insignificant compared to these.

Trimethylsilyl (TMS) Ether Derivatives

The mass spectra of the trimethylsilyl ether derivatives of 1- and 2-monomyristin are shown in Figure 3 and the intensities of relevant peaks are listed in Table III.

The spectra may be divided into hydrocarbon and silicon-containing peaks, the former being absent in the spectra at low electron voltage. The spectra of TMS ethers resembled those of the parent monoglycerides, but there was no similarity in the structures of the oxygen-containing ions of the monoglyceride spectra and the silicon-containing ions of the derivative spectra. Isomeric saturated monoglyceride TMS ethers gave spectra which were sufficiently different and characteristic to allow ready identification of the compounds, this being especially so at low electron voltages. Differences in the spectra of TMS derivatives of isomeric unsaturated monoglycerides were not so marked.

No parent ion peaks were observed in these spectra. The highest mass present in the spectra was the P-15 peak corresponding to the loss of a methyl radical from the parent ion. This has been found to be true for TMS ethers of relatively simple hydroxy compounds (5,18). In the case of large cyclic compounds (19) and some steroids (20), a parent ion peak may appear in the spectra of their TMS ether derivatives. This is probably because the positive charge is distributed over the cyclic system rather than being present on the oxygen-containing functional groups, providing greater stability to the parent ion. Reasoning from this basis, and from the spectra of the unsaturated monoglycerides, parent ion peaks might be expected to occur in the spectra of unsaturated monoglyceride TMS derivatives, but this was not found to be so.

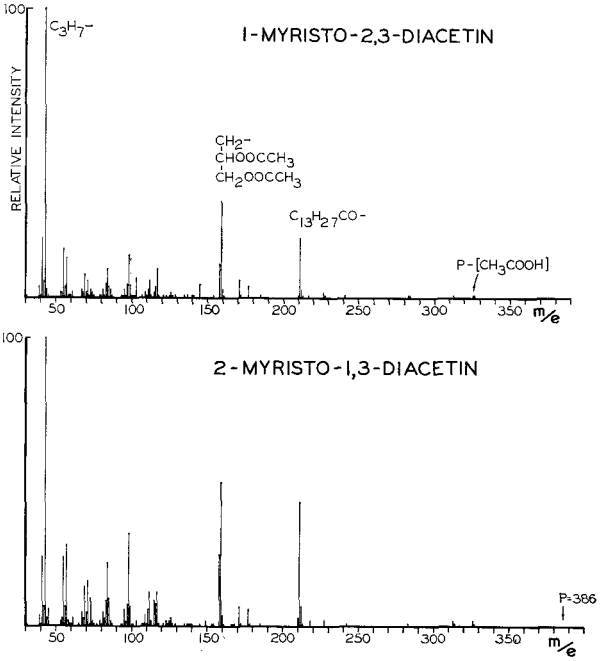


FIG. 2. Mass spectra of 1,2-diacetyl-3-myristin and 1,3-diacetyl-2-myristin.

TABLE II

Mass Spectra of Monoglyceride Diacetins

Fatty acid ion	MG[a]	10:0		12:0		14:0		16:0		18:0		20:0		18:1		18:2		18:3	
		H.V.[b]	L.V.[c]	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.
P—[CH_3COO]	1	1.7	2.5	....	....	0.9	40	2.7	10	27	100	...	7.3	0.5	3.6	....	....	....	....
" "	2	....	1.7	....	....	1.0	12	....	7.0	2.3	26	0.5	3.7	0.4	2.0	....	2.0	....	....
P—[CH_3COOH]	1	....	2.5	0.7	1.0	1.4	60	2.0	....	2.3	20	....	4.4	1.0	15	....	1.5	....	4.0
" "	2	....	4.6	....	....	2.2	52	0.6	12	6.4	95	0.6	8.7	0.9	3.0	....	30	....	....
P—[CH_3COOCH_2]	1	1.2	7.8	0.5	0.5	1.0	8.8	1.2	2.8	0.7	4.2	....	....	....	0.5	....	....	....	....
" "	2	2.7	22	0.7	....	2.4	37	....	....	0.6	21	....	1.4	....	1.3	....	....	....	....
P—[Long-chain acyloxy]	1	8.1	21	7.0	1.0	34	100	100	100	63	64	44	100	24	100	16	100	1.0	100
" "	2	14	25	5.5	1.1	50	100	24	100	71	100	71	100	16	85	7.8	100	11	90
P—[Long-chain acyloxy methylene]	1	2.2	7.2	2.0	0.5	4.5	10	11	12	6.0	6.2	3.9	7.8	1.6	2.5	2.9	12	2.0	8.0
	2	....	0.6	....	2.0	1.0	2.8	....	....	0.8	....	1.4	2.2	....	1.0	0.6	....	0.8	....
Acyl $CH_3(CH_2)_nCO$	1	13	19	6.6	1.0	21	48	35	28	21	18	1.8	11	3.6	11	....	2.5	....	....
" "	2	33	53	8.2	....	43	94	14	55	34	68	4.9	37	4.4	29	....	6.0	....	3.0
Acyl + 1	1	1.5	3.0	1.0	2.2	3.3	7.0	6.2	5.3	3.9	4.6	0.5	2.5	0.7	1.6	....	3.8	....	..
" "	2	3.9	7.0	1.3	1.0	6.6	15	2.4	10	6.6	16	1.2	8.1	0.8	4.0	....	....	1.4	100
$(CH_2)_nCO$	1	0.8	3.4	0.8	4.1	1.4	17	2.9	8.0	2.3	8.6	....	3.5	3.7	40	....	8.0	....	3.0
" "	2	1.0	5.5	0.6	3.5	2.5	18	1.0	7.0	4.8	30	0.6	5.4	3.4	100	....	35	....	4.0
Triacetin	1	....	2.5	4.4	4.8	....	....	1.1	....	1.3	5.5	....	2.4	....	..	....	1.2	..	4.0
"	2	0.5	5.5	0.5	2.5	1.6	21	0.5	35	3.0	25	0.6	2.3	0.7	0.8	....	....	...	2.0
CH_3COOCH_2	1	100	100	100	100	3.1	2.0	6.8	....	29	....	18	15	1.5	....	5.4	3.6	2.9	....
" "	2	68	100	100	100	9.7	1.1	2.3	17	28	15	5.4	....	2.4	0.8	3.1	....	3.6	2.5
C_3H_7	1	67	....	40	....	100	....	81	..	100	....	100	4.6	100	....	100	6.5	100	5.0
"	2	100	4.6	34	....	100	....	100	43	100	....	100	2.5	100	....	100	....	100	3.5

[a] MG = monoglyceride.
[b] H.V. = high electron voltage.
[c] L.V. = low electron voltage.

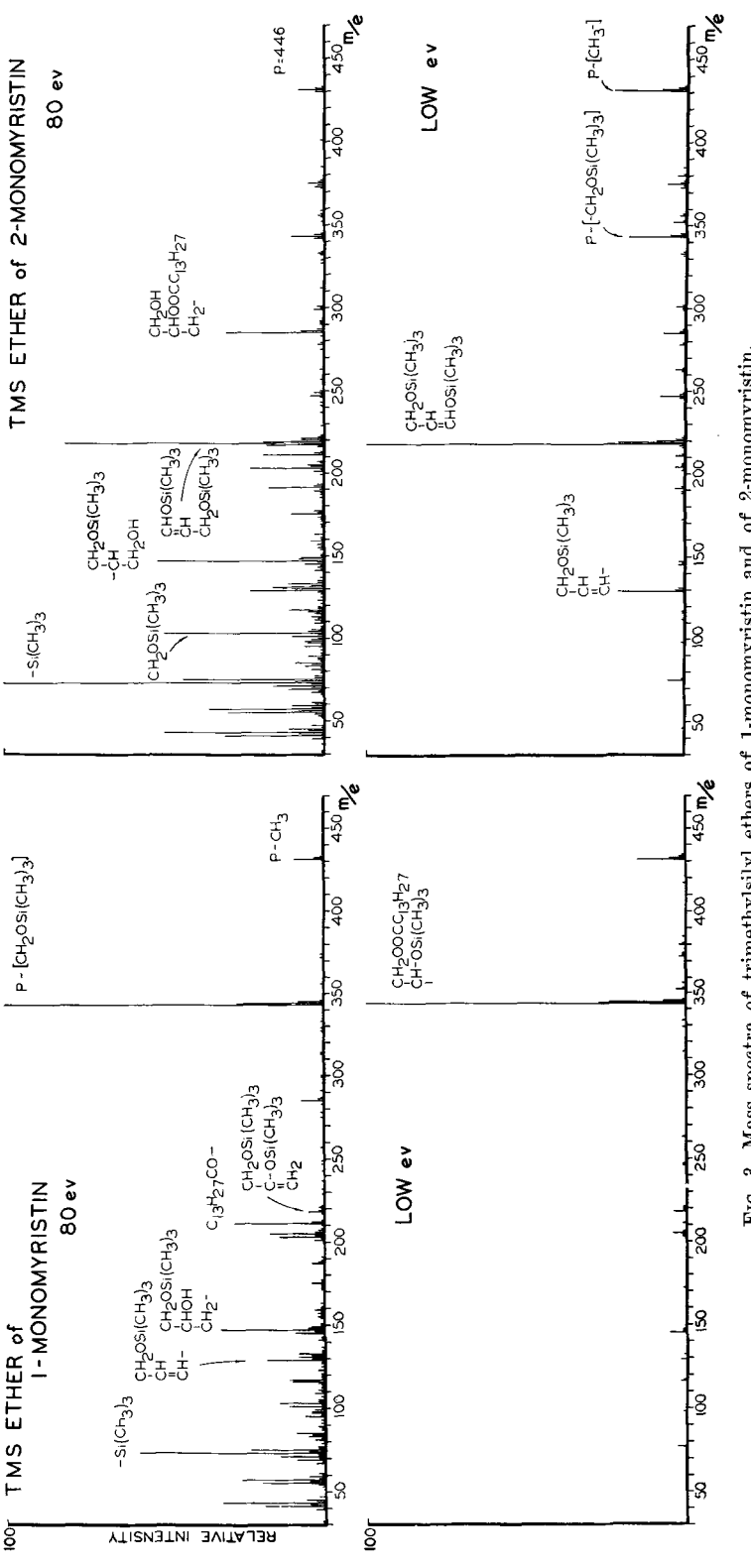


FIG. 3. Mass spectra of trimethylsilyl ethers of 1-monomyristin and of 2-monomyristin.

TABLE III

Mass Spectra of Monoglyceride TMS Derivatives

Fatty acid ion	MG[a]	10:0		12:0		14:0		16:0		18:0		20:0		18:1		18:2		18:3	
		H.V.[b]	L.V.[c]	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	L.V.
P—[CH_3]	1	7.9	14	8.8	12	8.6	15	3.5	15	8.3	17	3.3	12	4.4	31	2.3	11	0.6	....
" "	2	4.8	17	7.2	18	8.3	23	4.5	12	4.2	33	....	11	2.0	4.6	0.9	3.8	....	....
P—[CH_2O $Si(CH_3)_3$]	1	100	100	100	100	100	100	42	100	92	100	32	100	31	49	8.0	35	1.5	....
" "	2	3.7	10	4.0	12	10	18	3.8	7.8	3.2	2.2	0.7	18	2.9	8.2	....	0.8	....	....
m/e = 41	1	23	....	24	....	19	....	55	....	33	....	50	....	55	....	....	....	72	4.5
" "	2	21	....	28	....	31	....	33	....	23	....	39	....	62	1.0	61	....	100	....
m/e = 43	1	38	....	39	....	32	....	91	....	68	....	100	....	51	....	....	....	63	9.5
" "	2	33	....	42	....	50	....	57	....	45	....	65	....	52	1.5	34	....	70	....
m/e = 75	1	43	4.5	68	....	23	....	30	10	33	....	34	1.0	25	48	32	38	52	100
" "	2	38	22	40	3.5	44	4.8	33	....	25	....	28	....	39	17	43	2.3	47	100
m/e = 218	1	6.9	9.1	5.2	6.9	4.7	3.5	4.5	15	6.1	4.0	2.7	....	1.5	....	2.0	10	2.0	2.0
" "	2	53	100	82	100	81	100	63	100	76	100	63	100	11	33	8.8	27	3.5	3.0
m/e = 129	1	22	4.2	19	2.5	18	1.7	26	21	39	1.2	31	6.6	62	100	35	100	19	16
" "	2	74	15	98	26	23	21	92	7.0	100	5.1	100	43	22	100	72	71	20	26
$(CH_3)_3Si$	1	100	....	98	....	58	....	100	2.0	100	1.0	74	11	100	15	100	3.0	100	10
"	2	100	....	100	....	100	....	100	....	82	....	73	....	100	6.0	100	1.5	87	16
Acyl $CH_3(CH_2)_nCO$	1	63	1.9	38	0.8	28	1.0	23	22	23	1.0	14	4.1	13	28	6.3	24	2.4	3.0
" "	2	25	2.5	23	3.5	19	2.9	12	3.0	8.6	7.0	9.8	7.9	13	19	50	25	....	1.5
$(CH_2)_nCO$	1	....	....	....	....	0.7	....	....	1.2	0.8	....	....	....	2.6	23	6.3	70	2.1	3.0
" "	2	....	....	....	....	....	....	....	....	....	....	0.9	3.2	10	33	6.0	100	....	2.0
Acid	1	....	....	....	....	....	....	....	0.6	1.1	1.9	....	....	....	10	0.8	4.1	2.8	2.0
"	2	0.6	....	....	....	....	....	....	....	....	....	....	....	2.7	1.3	0.6	6.7	....	2.0
Acid + 1	1	9.5	1.4	8.3	....	7.2	7.0	1.3	2.2	7.4	1.3	....	....	....	9.0	16	3.8	5.9	3.0
" "	2	26	4.8	32	7.8	30	....	18	14	16	....	....	....	1.7	1.0	1.2	3.1	1.0	3.0

[a] MG = monoglyceride.
[b] H.V. = high electron voltage.
[c] L.V. = low electron voltage

Trimethylsilyl Ether Derivatives of Saturated Monoglycerides

Spectra at High Electron Voltage. Except for 1-monostearin, the base peak of TMS derivatives of 1-monoglycerides corresponded to fragments caused by the loss of methylene trimethylsilyl ether radicals, $-CH_2OSi(CH_3)_3$, from the parent ions. In the spectra of TMS derivatives of 2-monoglycerides, this peak was, in general, less than 10% of the base peak which was the trimethylsilyl radical (m/e = 73). The latter peak was also prominent in the spectra of the 1-monoglyceride derivatives. Loss of the acyloxy group to form an ion of m/e = 218 was more prominent in the spectra of the 2-monoglyceride derivatives than in those of 1-monoglycerides. Ions containing one silicon atom, having m/e = 219 and 147, were present in these spectra.

The intensity of the acyl ion was less in these spectra than in those of the parent monoglycerides. Peaks corresponding to the fatty acid and methyl ester were absent, though usually an ion was present corresponding to the acid-plus-one.

Spectra at Low Electron Voltage. The only peaks of significance in the spectra of TMS derivatives of 1-monoglyceride were those corresponding to the loss of methylene trimethylsilyl ether (base peak) or the methyl group from the parent ions. The base peaks in the spectra of 2-monoglyceride derivatives corresponded to the loss of the acyloxy group (m/e = 218). Three peaks of approximately equal intensity were present, corresponding to $P-[CH_3]$, $P-[CH_2-O-Si(CH_3)_3]$, and m/e = 129.

Trimethylsilyl Ether Derivatives of Unsaturated Monoglycerides

In all cases the base peaks in the spectra at high electron voltage corresponded to the trimethylsilyl radical, as was the case for the saturated monoglyceride TMS derivatives. No generalization may be made for the position of the base peaks at low electron voltages. Differences in the spectra of isomers were similar to those described above for the saturated compounds, though they were not as great.

Possible Analytical Applications of the Spectra

Because the differences in the spectra of 1- and 2-monoglycerides themselves were small and variable, this precludes the use of these for the analysis of monoglyceride mixtures. This was also found to be true for the diacetin derivatives of the monoglycerides. The trimethylsilyl ether derivatives show more promise in this respect, though the marked differences in the spectra of the saturated and unsaturated compounds is a disadvantage.

Spectra of TMS derivatives of monoglycerides can be used to distinguish the isomers. Moreover, the content of each isomer can be estimated, for the $P-[CH_2OSi(CH_3)_3]$ is a measure of the 1-monoglyceride, and the m/e = 218 is a measure of the 2-monoglyceride. The TMS derivatives of saturated 1-monoglycerides have comparable spectra and analysis of their mixtures is feasible by mass spectrometry. The same is true for TMS derivatives of saturated 2-monoglycerides. The analysis of monoglyceride mixtures by GLC-mass spectral analysis should be feasible.

Complete mass spectra of all compounds mentioned in this study are available upon request.

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