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GC/MS Analysis of Some Long Chain Esters, Ketones and Propanediol Diesters

M. VAJDI, W.W. NAWAR, Department of Food Sciences and Nutrition,
University of Mass., Amherst, MA 01003, and C. MERRITT, Jr.,
Food Sciences Laboratory, U.S. Army Natick Research and Development
Command, Natick, MA 01760

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ABSTRACT

Identification of radiolysis products which are formed in lipids in the range of molecular weights from 400-600 has been established on the basis of gas chromatography/mass spectrometry (GC/MS) studies of long chain authentic samples of alkyl esters, ketones and propanediol diesters. This paper describes the GC/MS behavior of these compounds. Double hydrogen rearrangement was found to be the predominant ion in the spectrum of long chain saturated esters whereas in the unsaturated esters, a peak corresponding to the loss of alcohol from the molecular ion was more pronounced. On the contrary to short chain ketones, McLafferty rearrangement did not appear to be the major fragmentation in the spectrum of saturated and unsaturated long chain ketones. α -Cleavage was found to be the predominant fragmentation in the spectrum of these ketones. The "McLafferty + 1" rearrangement peak was more pronounced for the long chain ketones than those found in the spectrum of smaller ketones. Fragmentation patterns of propanediol diesters were shown to be similar to those in triglycerides, giving rise to predominant peaks corresponding to acylium ion $[RCO]^+$ and parent minus acyloxy ion $[R-COO]^+$.

INTRODUCTION

The presence of long chain esters and diol diesters have been indicated in nature from various sources (1,2). In our studies of irradiated triglycerides and natural fats (3,4), certain long chain esters, ketones and propanediol diesters have been identified. The spectra of these compounds have not been studied or reported previously. This paper describes the gas chromatographic and mass spectrometric (GC/MS) behavior of these compounds.

MATERIALS AND METHODS

The reagents used for the preparation of compounds in this study were purchased from ICN, Pharmaceutical Inc., Plainview, NY. The purity of each product was established by GC.

Long chain esters (pentadecyl palmitate, pentadecyl oleate and hexadecenyl oleate) were synthesized by the reaction of the alcohol and the corresponding acid chloride in a solution of chloroform and pyridine.

The symmetrical ketone (16-hentriacontanone) and the monounsaturated ketone (18-tritriaconta-9-enone) were prepared according to the Gilman and Nelson method (5).

Propanediol diesters were prepared using 1,2-propanediol, and 1,3-propanediol with the appropriate acid chloride by the Baumann et al. method (1).

GC/MS data for all the compounds were obtained on a Dexil-400 column (operating conditions are given in Fig. 1) and a system composed of a PE Model 3920 gas chromatograph coupled to a Dupont Model 21-491 double focusing mass spectrometer via a glass jet molecular separator. Mass spectral data were acquired and analyzed by means of a data system employing HP Model 2116 and DEC PDP 15/76 computers.

RESULTS

The mass spectra of the long chain esters and ketones are shown in Table I. Some typical mass spectra are represented as histograms in Figures 2-5.

Gas chromatograms of the authentic isomers of propanediol diesters were obtained individually and as a mixture to obtain resolution and retention time data for comparison with those of the unknown mixtures analyzed in the radiolysis studies (3,4).

The gas chromatograms of the propanediol diesters demonstrated an adequate resolution between the synthesized isomers. 1,2-Propanediol diesters appeared before 1,3-propanediol diesters when separated on Dexil-400 column (Fig. 1).

The mass spectra of 1,2-propanediols were similar to those of 1,3-propanediols with respect to the fragmentation pattern. Table II presents the relative abundance of the major fragmentation ions obtained from propanediol diesters. The parent ions were not observed.

DISCUSSION

Because of the similarity of mass spectra within each group, only a few examples were chosen to be discussed here in detail.

Saturated Esters

In the spectra of short chain methyl esters, β -cleavage with a transfer of γ -hydrogen (McLafferty rearrangement) results in the formation of a characteristic base peak at m/e 74 (6). Although double hydrogen rearrangement occurs to a small

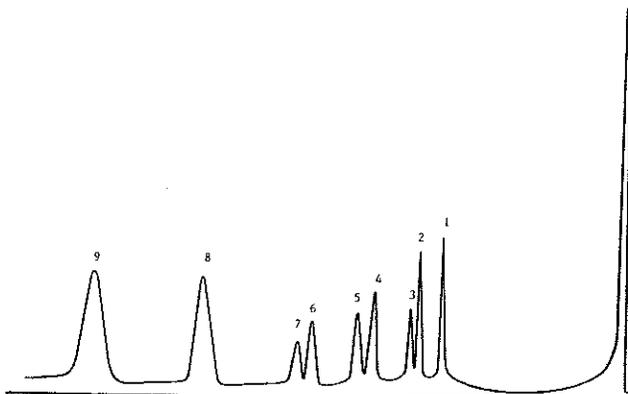


FIG. 1. Gas chromatogram of propanediol diesters. Column: 3% Dexil 400 (5' X 1/8"); temp.: 250 C-340 C (10C/min); flow rate: 30 ml/min. Peak No. 1 = 1,2-tetradecanoyl propanediol diesters; 2 = 1,3-tetradecanoyl propanediol diesters; 3 = 1,2-tetradecanoyl propanediol diesters; 4 = 1,3-tetradecanoyl propanediol diesters; 5 = 1,2-hexadecanoyl propanediol diesters; 6 = 1,3-hexadecanoyl propanediol diesters; 7 = 1,2-hexadecanoyl pntadecenoyl propanediol diesters; 8 = 1,2-octadecenoyl propanediol diesters; 9 = 1,3-octadecenoyl propanediol diesters.

TABLE I

Relative Abundance of Ions in the Mass Spectra of Some Long Chain Esters and Ketones

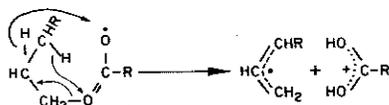
Compound ^a m/e	Esters					Ketones			
	1	2	3	4	5	6	7	8	9
41				60					
43	80	100	98		92	97	100	55	100
55			100	100					
57	82	85			90	98	90	48	80
58					58	70	80	30	22
69			82	96					55
71	55	70			100	100	98	40	
83	60	62	80	85					38
85					55	58	68	20	
96					45	47	50	18	
97	48	64	65	80					40
100									
111	30	18	41	15					
124				48					
125	22		24						
138				38					
182	13	4							
183					10	5			
210	40								
211					90 α	56 α		7	
222			20	50					
224		16							
225							80		
226					25M	15M			
227					40H	30H			
237									10
239	20	55			12 γ	50 α	94 α	100 α	35 α
240							45		
241							38H		
253					5				
254						15M	28M	35M	
255	10	22				17H	35H	62H	18H
257	100r	52r							
264			90	32					
265				38					30 α
267						10r	15 γ	18 γ	12 γ
268							25		
283			25r	15r					5H
293									5 γ
307									15
321									32
394					2P				
422						4P			
436							5P		
449									12
450								10P	
466	52P								
476									2P
480		18P							
492			12P						
504				8P					

^a1 = Pentadecyl palmitate (MW 466); 2 = Hexadecyl palmitate (MW 480); 3 = Pentadecyl oleate (MW 492); 4 = Hexadecenyl oleate (MW 504); 5 = 14-Heptacosanone (MW 394); 6 = 14-Nonacosanone (MW 422); 7 = 15-Triacontanone (MW 436); 8 = 16-Hentriacontanone (MW 450); 9 = 18-Tritriacontanone (MW 476); H = McLafferty + 1 rearrangement; r = double hydrogen rearrangement; α = alpha cleavage; γ = gamma cleavage; P = Parent ion; M = McLafferty rearrangement ion.

extent in the short chain compounds, it becomes predominant with an increase in the aliphatic alkyl chain beyond the propyl group (7), and replaces the McLafferty rearrangement ion as the most abundant ion.

The predominant double hydrogen rearrangement peak in the mass spectrum of the esters of long chain alcohols and long chain fatty acids may be depicted as a decomposition of the odd electron parent ion with rearrangement of two hydrogen atoms (Scheme I).

SCHEME I



The process accounts for the base peak of m/e 257 in the spectrum of pentadecyl palmitate and an abundant peak in the spectrum of hexadecyl palmitate (Fig. 2). The hydrogen-type peaks at m/e 210 and 224 [M-256] in each of the saturated palmitate esters correspond to a loss of the acid moiety. Similar peaks were observed by Ryhage and Stenhagen (6) in the spectra of other long chain saturated esters. Other peaks may be expected at M-(RCOOH + 28). A distinct molecular ion is present as well as a peak at m/e = [M-211], indicating cleavage at the acyloxy site.

Unsaturated Esters

In the mass spectra of pentadecyl oleate, the predominant major fragmentation typical of unsaturated esters is found

TABLE II

Relative Abundance of Principle Ions in the Mass Spectra of Propanediol Diesters

Compound ^a :	1	2	3	4	5	6	7	8	9	10	11
m/e	Intensity										
41								10			18
43	98	90	60	45	70	35	27		78	55	
55								15	76		48
57	82	55	64	34	68	25	28			58	
69									60	38	44
71	63	20	45	20	45	20	17	12			
84	50	38	45	15	50	18	4	5	38	35	12
98	50	25	58	18	55	19	5	15	56	38	22
100	55	40	68	26	70	18	10	12	62	35	12
113	52	42	60	25	65	30	25	30	65	50	28
169	25	15	25	10	25	12	18	10	25	15	12
211	98	85	50			30					
229	22	8	4			4					
239		60	45	70	55		25	15	50		
257		12	2	10	3		3	2	5		
264						35		20	75	25	15
265						20		18	44	15	30
267							15			32	
269	100	100	100			100					
283						2		5	2	1	
285							2			2	
287	45	15	25			12					
297		95	98	100	100		100	100	85		
315		12	10	12	20		8	2	25		
322						45			98	35	42
323						50		38	100	50	100
325							25			100	
341						3		2	1	2	4
343							5			2	

^a1 = 1,2-Tetradecanoyl propanediol diesters (MW 496); 2 = Tetradecanoyl hexadecanoyl 1,2-propanediol diesters (MW 524); 3 = Tetradecanoyl hexadecanoyl 1,2-propanediol diesters (MW 524); 4 = 1,2-hexadecanoyl propanediol diesters (MW 552); 5 = 1,3-Hexadecanoyl propanediol diesters (MW 552); 6 = Tetradecanoyl octadecanoyl 1,3-propanediol diesters (MW 550); 7 = Hexadecanoyl octadecanoyl 1,2-propanediol diesters (MW 580); 8 = Hexadecanoyl octadecanoyl 1,2-propanediol diesters (MW 578); 9 = Hexadecanoyl octadecanoyl 1,3-propanediol diesters (MW 578); 10 = Octadecanoyl octadecanoyl 1,3-propanediol diesters (MW 606); 11 = 1,2-Octadecanoyl propanediol diesters (MW 604).

at m/e 264 due to the apparent loss of a fragment corresponding to the alcohol group [M-288]. This behavior is similar to the apparent loss of methanol from methyl oleate when M-32 becomes the base peak in that spectrum (6). Another characteristic peak is seen at m/e 222 [M-270] corresponding to a similar peak found in methyl oleate [M-74]. The lost species may be postulated to be a rearrangement fragmentation of the McLafferty type, with cleavage β to the carboxyl and a transfer of hydrogen to the carboxyl, where the charge remains on the alkenyl residue rather than the carboxyl moiety. Double hydrogen rearrangement also occurs, but to a lesser degree (25%) than with saturated esters yielding a peak at m/e 283 (Table I).

The apparent loss of alcohol is similarly evident in the mass spectrum of hexadecenyl oleate (Fig. 3), producing a peak at m/e 264. Cleavage at the acyl site produces a large peak at m/e 265, whereas the peak at m/e 222 corresponds as in pentadecyl oleate to β -cleavage [M-282] with hydrogen transfer to the carboxyl.

Ketones

α -Cleavage is a predominant fragmentation in the spectra of long chain ketones (Table I), yielding the acyl ion (RCO or, i.e., M-R). It produces the base peak in a symmetrical ketone such as palmitone (16-hentriacontanone). In an unsymmetrical ketone such as 15-triacontanone, the cleavage,

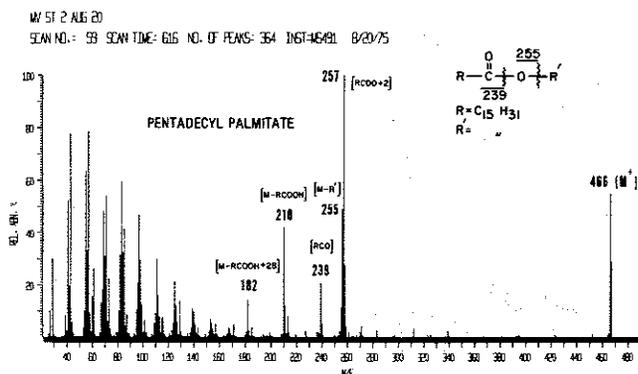


FIG. 2. Mass spectrum of pentadecyl palmitate.

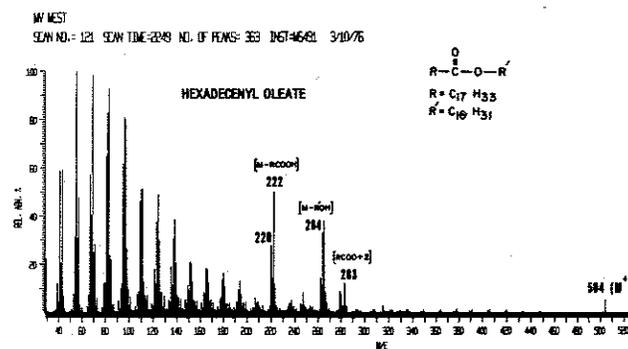
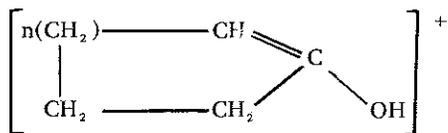


FIG. 3. Mass spectrum of hexadecenyl oleate.

as the corresponding acylium ion $[RCO]^+$ (Fig. 5).

In all cases, a distinct pattern of fragmentation was noted for all the propanediol diesters studied. A base peak corresponding to the ion $[M-RCOO]^+$ was observed in all the spectra obtained. Another fragmentation typical of propanediol diesters is due to a common ion of the structure:



and giving rise to m/e 84 and 98 corresponding to n of 1 and 2, respectively. Additional peaks of low intensities (287, 315, 341, 343) arising from the loss of the acyl group from the compound and capture of two hydrogens also were found in the spectra (Table II). In general, the pattern of fragmentations obtained in the spectra of propanediol diesters was in agreement with those of ethanediol diesters reported previously (2).

ACKNOWLEDGMENT

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