

DETERMINATION OF OIL FFA BY GLC

TABLE III

Free Fatty Acid Composition in Vegetable Oils as Determined by the New Procedure (mean \pm SD n = 6)

	Composition of free fatty acids (%)			
	Safflower seed oil	Soybean oil	Corn oil	Cottonseed oil
16:0	8.6 \pm 0.18	17.8 \pm 0.58	12.8 \pm 0.28	25.2 \pm 0.19
18:0	4.5 \pm 0.22	18.5 \pm 0.51	3.7 \pm 0.19	3.4 \pm 0.06
18:1	12.6 \pm 0.12	43.0 \pm 0.85	25.1 \pm 0.18	18.6 \pm 0.10
18:2	72.2 \pm 0.50	20.6 \pm 1.43	56.7 \pm 0.35	52.9 \pm 0.21
		Wt % ($\times 10^{-4}$)		
16.0	23.9 \pm 1.40	16.6 \pm 1.06	36.8 \pm 1.60	365.5 \pm 4.00
18:0	12.6 \pm 2.70	17.3 \pm 0.88	10.8 \pm 0.80	49.7 \pm 1.30
18:1	35.3 \pm 2.70	40.2 \pm 1.88	72.3 \pm 2.80	270.6 \pm 4.10
18:2	201.9 \pm 15.90	19.2 \pm 1.07	163.4 \pm 6.00	769.3 \pm 12.00
Total	279.3 \pm 20.50	93.5 \pm 3.45	288.0 \pm 10.9	1455.1 \pm 20.20

It is best to prepare the sample and do the chromatographic analysis in the same day. This prevents analysis of any glyceride fatty acids that may be made from traces of glyceride left on the walls or at the interface.

This new procedure for the determination of free fatty acids in vegetable oils overcomes difficulties presented by other procedures in the literature. The new procedure is rapid, simple, highly sensitive and gives quantitative results for the individual fatty acids as well as a measure of the total amount of free fatty acid. Furthermore, the partitioning of the free fatty acids from the vegetable oil allows repeated injections into a gas chromatograph without destruction of the column by glyceride contamination. This new procedure should be useful in determining the free fatty acid content in commercial in-process oils and in oilseeds.

ACKNOWLEDGMENT

This work was supported by the Veterans Administration.

REFERENCES

1. Official and Tentative Methods of the American Oil Chemists' Society, 3rd edn., Vol. 1 and 2, AOCS, Champaign, IL, 1964 (revised to 1972), Method Ca5a-40.
2. Ottenstein, D.M., and W.R. Supina, J. Chromatogr. 91:119 (1974).
3. Chapman, G.W., Jr., JAOCS 56:77 (1979).
4. D'Alonzo, R.P., W.J. Kozarek and H.W. Wharton, JAOCS 58:215 (1981).
5. MacGee, J., and K.G. Allen, J. Chromatogr. 100:35 (1974).
6. Williams, M.G., and J. MacGee, Ibid. 234:468 (1982).

[Received May 28, 1982]

A Quantitative Study of the Pathways Involved in the Formation of Radiolysis Products in Ethyl Palmitate

C. MERRITT, JR., M. VAJDI¹, M.L. BAZINET and P. ANGELINI, Science and Advanced Technology Laboratory, US Army Natick Research and Development Laboratories, Natick, MA 01760

ABSTRACT

The various compounds produced by irradiation in ethyl palmitate have been determined by direct mass spectrometry and gas chromatography mass spectrometry. Postulated mechanisms for their formation have been confirmed by a comparison of product yields, and a material balance is shown between the G-values for products and their putative precursors. The total product yield is seen to be nearly equal to the amount of radiation absorbed. Three new radiolysis products, viz. ethyl α -ethylpalmitate, ethyl hexadecen-2-oate and butyl palmitate are reported.

INTRODUCTION

The various compounds formed in meats (1-12), triglycerides (2,4,5,9,12-21), fatty acids and fatty acid esters (4,9, 12,16-18, 20-25) have been well characterized by qualitative analysis employing mainly mass spectrometry (MS). Quantitative methods have also been devised (1,3,9,12,26-29) allowing determination of the relative amounts of these components, and the reaction pathways have been adduced or proposed (16,17,19,30).

¹Visiting Scientist, Department of Food Science & Nutrition, University of Massachusetts, Amherst, MA 01003.

Since a variety of compounds are formed in varying amounts, it has seemed desirable to establish a means of measuring the favored reactions and establish a material balance for the distribution of energy absorbed in the radiation process. Accordingly, a scheme has been devised to measure the yield of all the possible radiation products formed in a single substance and, if possible, account for their distribution. For reasons described in detail below, ethyl palmitate was chosen as the test substance. The results are presented in this manuscript.

EXPERIMENTAL

Practical grade ethyl palmitate was obtained from Eastman Kodak Co., Inc., (Rochester, NY) and purified by spinning band distillation to remove trace amounts of esters of other fatty acids and other high boiling impurities. The purity was checked by gas chromatography (GC) under the same conditions used for subsequent analysis. Complete removal of compounds having boiling points close to that of ethyl palmitate was not achieved, but the impurities remaining were found not to interfere in the analysis (see Figs. 1 and 2). Volatile impurities were removed from ethyl palmitate

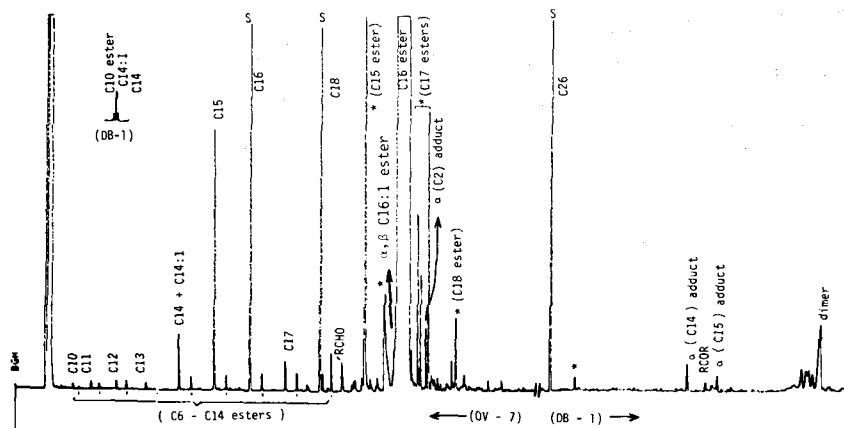


FIG. 1. Gas chromatogram showing separation of radiolysis products of ethyl palmitate at 25 Mrad and 30 C. Column: 0.32 mm \times 60 m FSOTBP; left side OV-7, right side DB-1. Helium carrier gas, 2 mL/min. Temperature, 100 C to 320 C @ 4 C/min. Inset: Separation of certain components on DB-1. Hydrocarbons indicated as C_n, ethyl esters as C_n ester where n is the carbon number of the fatty acid. Other compounds indicated by functional group where R = C₁₅. S = internal standard, * denotes an impurity in the ethyl palmitate used.

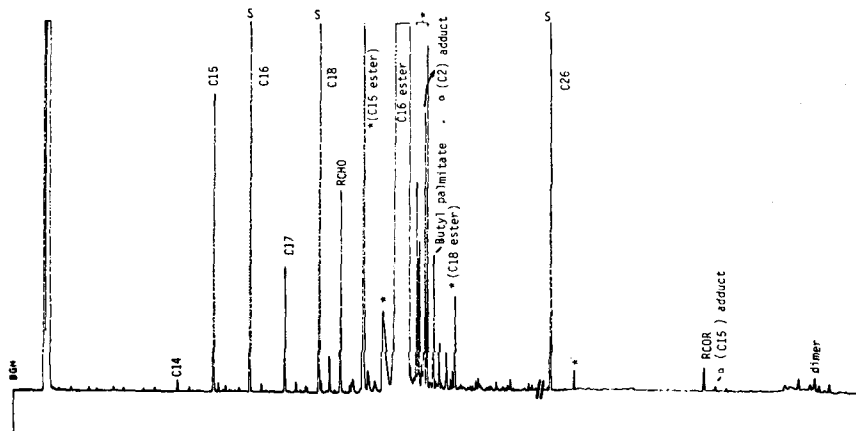


FIG. 2. Gas chromatogram showing separation of radiolysis products of ethyl palmitate at 25 Mrad and -45 C. Column: 0.32 mm \times 60 m FSOTBP; left side OV-7, right side DN-1. Helium carrier gas, 2 mL/min. Temperature, 100 C to 320 C @ 4 C/min. Hydrocarbons indicated as C_n, ethyl esters as C_n ester where n is the carbon number of the fatty acid. Other compounds indicated by functional group where R = C₁₅. S = internal standard, * denotes an impurity in the ethyl palmitate used.

prior to irradiation by evacuation at 10^{-3} Torr in the irradiation tube fitted with break seals before sealing (3,26). Irradiation was carried out in a Co⁶⁰ source to provide a dose of 25 Mrads. Two conditions of temperature were chosen to provide for irradiation of the ethyl palmitate in the liquid state (30 C) and in the solid state (-45 C). The relatively high dose was employed to ensure the formation of low level components in sufficient amounts for accurate measurements.

Determination of the volatile compounds produced was accomplished by direct mass spectrometry on a CEC Model 21-103 mass spectrometer by well established methods (1,3,26-29,31) of headspace and total condensate analysis.

The higher molecular weight components were determined by gas chromatographic separation and analysis by injection of the ethyl palmitate dissolved in CHCl₃ (1:1, v/v). Since not all of the components could be determined on a single column, the GC analyses were performed on three columns. Most of the compounds were separated and determined by measurement of integrated peak areas on a 0.32 mm \times 60 m fused silica open tubular bonded DB-1

phase (FSOTBP/DB-1) column. The column was especially efficacious for the separation of the several adduct compounds that were found not to be completely separated on packed columns. Corresponding determinations of most of the compounds were also made, however, on two other columns since three key compounds, viz. palmitic acid, palmityl aldehyde, and the α -ethyl adduct compound, could not be determined on the FSOTBP/DB-1 column. Palmitic acid was determined on a 1/8 in. \times 6 ft column coated with 10% FFAP (Terphthalate-Carbowax 20M) on 80-100 mesh Chromasorb W, and palmityl aldehyde and ethyl α -ethyl-palmitate were determined uniquely together with duplicate determinations of several other components (see Table I), on a FSOTBP/OV-7 column. Hexadecane, octadecane and hexacosane were used as internal standards in all of the determinations. Response factors were measured for all of the components for which authentic standards were available (i.e., except the adduct compounds) and all were found to be of nearly equal magnitude. In subsequent calculations, all response factors were assumed to be equal and all determinations are based on relative peak areas measured by a

RADIOLYSIS PRODUCTS IN ETHYL PALMITATE

TABLE I
G-Values^a Determined for Radiolysis Products from Ethyl Palmitate

Compound	Irradiation @ 30 C			Irradiation @ -45 C		
Compounds determined by direct mass spectrometric analysis of headspace or condensate at -196 C						
Hydrogen	2.17			2.14		
Carbon monoxide	0.10			0.02		
Methane	0.07			0.02		
Carbon dioxide	0.18			0.16		
Ethene	0.09			0.02		
Ethane	0.70			0.90		
Propene	0.01			0.01		
Propane	0.26			0.08		
Butane	0.04			0.04		
Ketene	0.01			—		
Ethanol	0.25			0.22		
Ethyl formate	0.05			—		
Ethyl acetate	0.02			0.01		
Compounds determined by GC						
	column			column		
	DB-1	OV-7	FFAP	DB-1	OV-7	FFAP
^b Tetradecene	0.07	0.08	0.08	t	—	t
^b Tetradecane	0.01	—	—	t	t	t
^b Pentadecane	0.38	—	—	0.28	0.28	—
^b Heptadecane	0.04	0.04	0.03	0.10	0.10	0.14
^b Hexadecanal	—	0.04	0.04	—	0.20	0.18
^c Ethyl α -ethylpalmitate	—	0.07	—	—	0.19	—
^c Butyl palmitate	0	0	—	0.10	0.10	—
^d Octacosane	t	—	—	t	—	—
^d Triacontane	t	—	—	t	—	—
^c Ethyl α -tetradecylpalmitate	0.02	0.05	—	0	0	—
^b Dipentadecyl ketone	0.01	0.03	—	0.01	0.03	—
^c Ethyl α -pentadecylpalmitate	0.01	0.03	—	t	t	—
^c Ethyl palmitate α,α' dehydrodimer	0.60	—	—	0.60	—	—
^b Palmitic acid	—	—	0.9	—	—	1.0
^c Ethyl α,β hexadecenoate	—	0.10	—	—	—	—

^aSymbols as follows: t: <0.01, 0: not found, dash: indeterminate, blank: not measured.

^bConfirmed by retention time and mass spectrum of authentic compound.

^cConfirmed by interpretation of mass spectrum.

^dIndicated by retention time of authentic compound.

digital integrator. All G-values except for the volatiles and palmitic acid were computed from the capillary column data. All determinations were made on duplicate samples of irradiated ethyl palmitate for each temperature condition. All data given in Table I represent, therefore, averages of two determinations. Typical fused silica column chromatograms are shown in Figures 1 and 2. Operational parameters are given in the legends.

The identity of all the radiolytic compounds was confirmed by retention time of corresponding authentic compounds and/or mass spectrometric identification of the eluting components on a GC-MS system. A Perkin-Elmer Model 3920 gas chromatograph coupled by means of a jet separator to a CEC/DuPont Model 21-491 mass spectrometer was used to identify eluates from the FFAP column. Chromatograms were acquired from the GC-MS system by means of a dual output that provided both a flame ionization response (from an effluent carrier gas splitter) and a mass spectrometer total ion current response (ion beam monitor).

Mass spectral data were acquired by means of a combined computer data system employing Hewlett-Packard Model No. 2116B and Digital Equipment Corporation Model No. PDP 15/76 computers. Reconstructed total ionization chromatograms corresponding to the analog chromatograms were generated and the components identified from spectra selected from appropriate mass spectrum scan numbers corresponding to the selected chromatographic peak. Where

possible, identification was confirmed by comparison with the spectra of authentic compounds (Table I).

Components separated on the FSOTBP/DB-1 column were identified by means of a Finnigan Model OWA GC-MS system. Aliquots of the irradiated ethyl palmitate samples were run on the same columns as used in the GC determinations with flame ionization detection (FID) and chromatograms were compared to establish the equivalent behavior of the two systems.

Three new radiolysis products were identified in this study. An ethyl α -ethylpalmitate analogous to the α -tetradecyl and α -pentadecyl adducts previously reported (31) was found to elute on FSOTBP/OV-7 between ethyl palmitate and ethyl stearate (see Figs. 1 and 2). The corresponding mass spectrum (Fig. 3) was found to exhibit a molecular ion at m/e 312 and McLafferty ions at 116 and 284. The compound was not observed previously because it coelutes on FSOTBP/DB-1 with ethyl heptadecanoate, an impurity in the ethyl palmitate. Its presence was confirmed, however, by computer deconvolution of the peak on FSOTBP/DB-1 by plotting selected ion chromatograms.

Ethyl hexadecen-2-oate was identified as a leading shoulder on the ethyl palmitate peak eluting from FSOTBP/DB-1. From GC-MS data, computer-generated selected ion chromatograms using mass peaks attributable to the unsaturated compound and ethyl palmitate showed the compound to be a nearly completely separated component. Specific mass peaks for the compound used in the identification were m/e

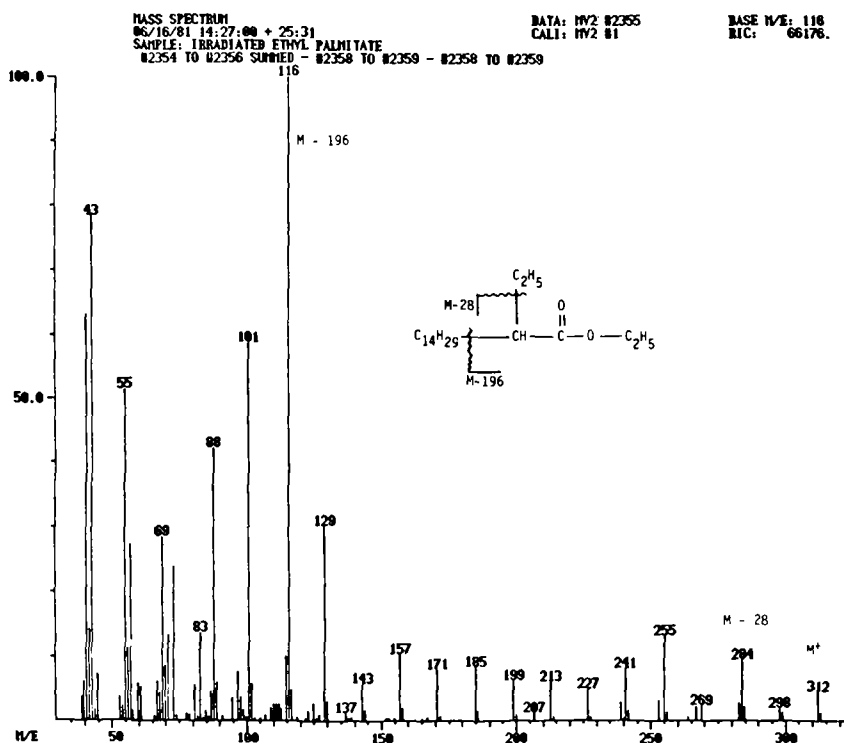


FIG. 3. Mass spectrum corresponding to gas chromatographic peak in Figures 1 and 2 identified as ethyl α -ethylpalmitate.

282 (M^+), m/e 236 ($M-C_2H_5OH$), and m/e 127 ($M-C_{11}H_{23}$; 5,6 cleavage). The mass peaks observed corresponded to similar peaks found in the spectra of other α,β unsaturated fatty acid esters reported in the literature (30,32). The selected ion chromatograms showed the presence of peaks due to the unsaturated ester over a range of scan numbers preceding the appearance of the molecular ion peak for ethyl palmitate, m/e 284. The respective molecular ions, i.e., m/e 282 and 284, were found to overlap by only 5 scans (i.e., 5 sec elution time). Accordingly, the amount of ethyl hexadecen-2-oate was determined by integration of its corresponding peak area on the deconvoluted chromatogram.

An additional recombination product of a type not previously reported, viz. butyl palmitate, was discovered to be formed in the radiolysis of ethyl palmitate at -45 C. Its elution position is shown in the chromatogram in Figure 2 and the corresponding mass spectrum is shown in Figure 4. The spectrum agrees in all structural aspects with the corresponding spectrum of its homolog, butyl stearate, which has been given in the literature (33). A deuterated homolog having significant ions in its spectrum at 118, 241 and 259 was observed for a GC eluate having the same retention time among the separated components of ethyl α,α' -dideuteropalmitate irradiated at -45 C (31).

RESULTS AND DISCUSSION

Ethyl palmitate was found to be an ideal system for the elucidation of the various radiolytic reaction mechanisms and the resulting products. As an ester it behaves in almost every respect as a triglyceride. Since it is normally a liquid, the quantitative relationships may differ slightly in some respects from solid triglycerides or esters (21). For comparison, data were also acquired in this study for ethyl palmitate in the frozen state.

From an analytical viewpoint, since the higher molecular weight products have sufficient volatility to separate on

a gas chromatograph, all but the very volatile radiolysis products may be determined by GC. The products, moreover, may be unequivocally identified by mass spectrometry.

The various reaction pathways and the resulting products are depicted in Figure 5. Two principal pathways are seen to produce the radiolysis products. In one, electron attachment results in a radical anion which upon dissociation gives the fatty acid anion and, ultimately, the free acid plus the ethyl free radical. An alternative dissociation of the radical anion may yield pentadecyl free radical and ethyl formate (vide infra). The other pathway involves the excited state ester molecule, arising directly from irradiation or by electron capture by a positive ion species (34). The excited state molecule may dissociate in a number of ways. Cleavage at the acyl position leads to ethanol and the acyl radical, which in turn dissociates to the pentadecyl free radical and carbon monoxide. Alternatively, cleavage at the acyloxy position leads to the acyloxy free radical which subsequently dissociates to carbon dioxide and the pentadecyl radical.

The fate of the various free radicals thus formed may be discerned from the G-values of the resulting products. Recombination and disproportionation of the alkyl radicals appear to be minor reactions, since only a slight amount of butane and a trace of triacontane are found, and no pentadecene and only a small amount of ethene are found. It thus appears that the main reaction of the alkyl free radicals is to abstract hydrogen from the parent molecule, ethyl palmitate, to yield the corresponding hydrocarbons and the ethyl palmitate free radical with an odd electron site α to the carboxyl. In a similar way, the acyl free radical abstracts to give an aldehyde and the ethyl palmitate free radical. The postulated mechanism is confirmed by electron spin resonance (ESR) measurements (35) in which the predominant free radical observed in the system is that of the so-called ethyl palmitate α abstraction radical. This arises not only by abstraction of hydrogen by alkyl and alkoxy

RADIOLYSIS PRODUCTS IN ETHYL PALMITATE

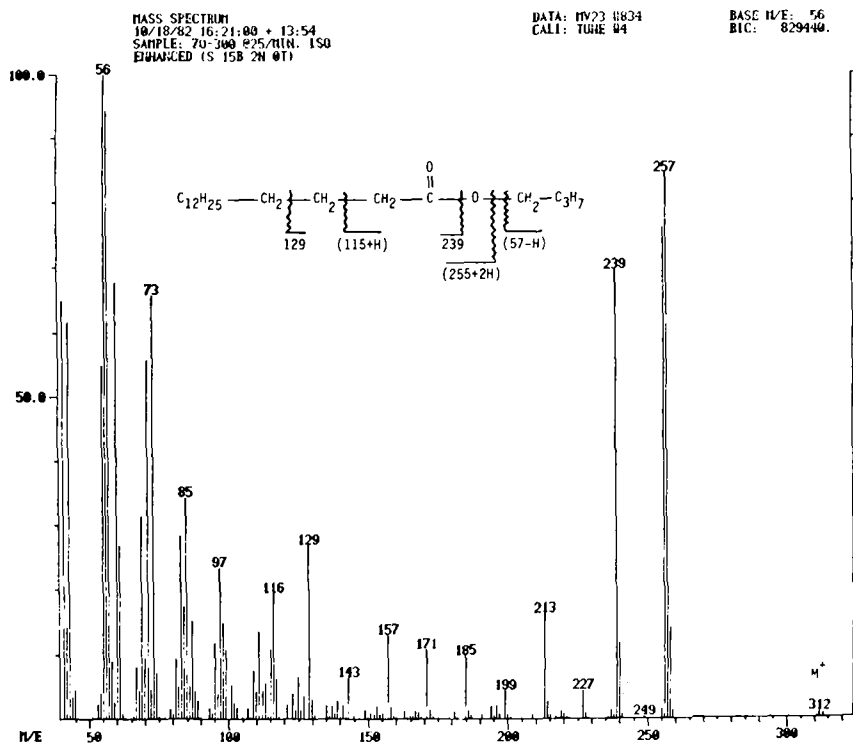


FIG. 4. Mass spectrum corresponding to gas chromatographic peak in Figure 2 identified as butyl butyrate.

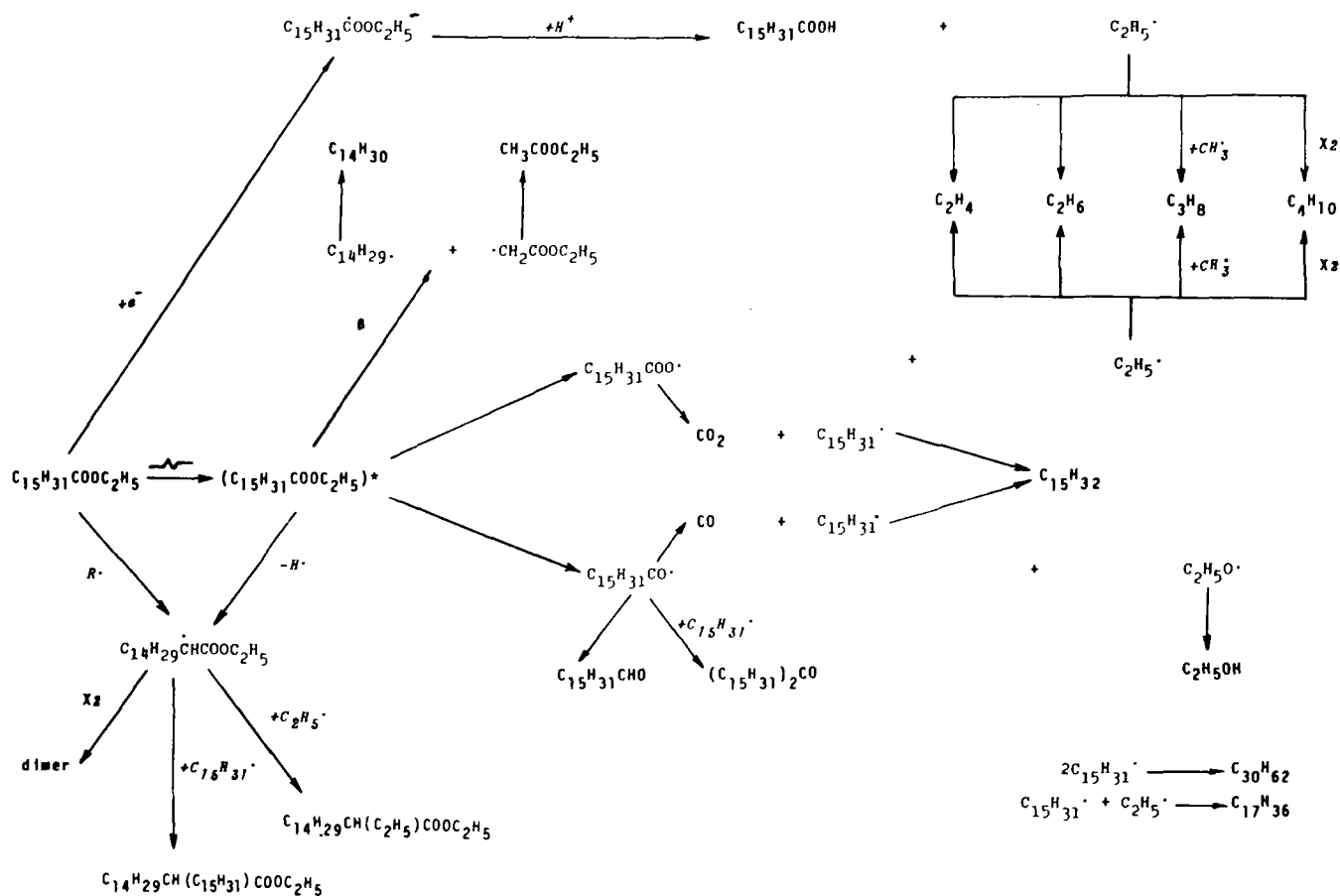
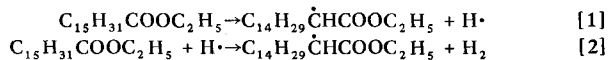
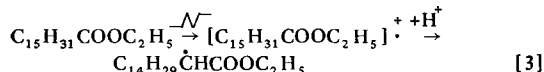


FIG. 5. Pathways for formation of radiolysis products in ethyl palmitate. G-values are given in Table I. (Formation of $C_{14}H_{29}CHOOC_2H_5$ via deprotonation of a positive radical ion is not shown.)

free radicals, but by dissociation of hydrogen from the excited state molecule itself:



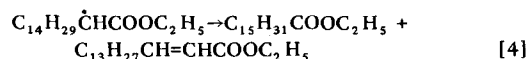
or by deprotonation of an ethyl palmitate positive radical ion.



The fate of the ethyl palmitate free radical is seen to be involved primarily in recombination reactions. Two types of products predominate. A dimer is formed, and other products result from the recombination of ethyl palmitate free radical with the various alkyl radicals yielding an ethyl α -alkyl branched palmitate. Identification of the dimer, an ethyl α -tetradecylpalmitate and the ethyl α -pentadecylpalmitate have been previously reported (31). Identification of ethyl α -ethylpalmitate is reported in this study.

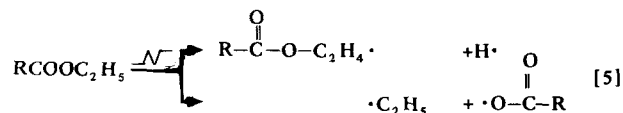
The formation of analog adduct compounds has been observed in studies of radiolysis products from tributyrin and tripalmitin (20). In these cases tributyrin and tripalmitin dimers and an adduct of the triglyceride and the corresponding propanedioldiester have been identified.

Evidence for the disproportionation reaction



is also seen by the occurrence of ethyl hexadecen-2-oate.

Another recombination product, butylpalmitate, was obtained in good yield ($G = 0.10$) at -45°C , but was not found as a radiolysis product at 30°C . A mechanism may be postulated in which primary free radicals formed in the cold and immobilized in the solid matrix are terminated by recombination of closely neighboring free radicals (ester groups are associated in the solid state).



The extent to which reaction occurs by the different pathways is seen by consideration of the G -values for the products. G -values for all the compounds determined are given in Table I. The amount of the precursor free radical for the several products formed at 30°C and -45°C may be estimated from the various stoichiometries as seen below (see Figure 5 for the corresponding reaction pathways).

For ethyl radical:

$$\begin{aligned} G(\text{C}_2\text{H}_5\cdot) &= G(\text{C}_{15}\text{H}_{31}\text{COOH}) + G(\text{CO}_2) \\ &= 0.9 \quad + \quad 0.18 = 1.08 \quad (30^\circ\text{C}) \\ &= 1.0 \quad + \quad 0.16 = 1.16 \quad (-45^\circ\text{C}) \end{aligned}$$

For pentadecyl radical:

$$\begin{aligned} G(\text{C}_{15}\text{H}_{31}\cdot) &= G(\text{CO}) \quad + \quad G(\text{CO}_2) \\ &= G(\text{C}_2\text{H}_5\text{OH}) - [G(\text{C}_{15}\text{H}_{31}\text{CHO}) + G(\text{C}_{15}\text{H}_{31}\text{COC}_{15}\text{H}_{31})] \\ &\quad + G(\text{CO}_2) \\ &= 0.25 \quad - \quad [0.04 + 0.03] \quad + \quad 0.18 = 0.36 \quad (30^\circ\text{C}) \\ &= 0.22 \quad - \quad [0.20 + 0.02] \quad + \quad 0.16 = 0.16 \quad (-45^\circ\text{C}) \end{aligned}$$

(A reliable G -value for CO was not obtained.)

The total amount of ethyl free radical precursor is computed from the contributions resulting from the formation of palmitic acid by electron attachment and from the carbon dioxide produced by dissociation of the palmytyloxy

free radical. Likewise, the amount of pentadecyl free radical is estimated from the dissociation of the acyloxy and acyl free radicals. Since a reliable determination of the amount of carbon monoxide could not be obtained, the contribution from acyl radical dissociation was deduced from the difference in G -values for ethanol and the combined G -values of palmitaldehyde and palmitone.

In the -45°C sample the difference between ethanol and palmitaldehyde/palmitone showed no contribution to the pentadecyl radical from acyl radical dissociation. This is consistent with previous observations (21) that termination of the acyl radical to form the aldehyde is a preferred pathway at low temperature.

The G -values for the several compounds postulated to be derived from the ethyl and pentadecyl free radicals are summarized in the piecharts shown in Figure 6. Although the amount of palmitic acid for purposes of calculation is taken to be derived from the ethyl palmitate radical anion formed from electron attachment, some may actually be produced by abstractions of hydrogen by the palmytyloxy free radical. The G -value for the corresponding ethyl radical, however, is not affected by the assumption, since whatever the proportion derived by either mechanism, ethyl free radical is given by the sum of the G -values for palmitic acid and carbon dioxide. Excellent agreement is seen for the compounds derived from the ethyl radical.

In the case of the liquid sample, compounds derived from pentadecyl radical show a good but lesser agreement than the ethyl radical derived compounds. This is a somewhat unexpected result since the accuracy of the G -values for compounds determined by gas chromatography (i.e., pentadecane, palmitaldehyde, palmitone, etc.) must be regarded as higher than that for the volatile compounds determined by direct mass spectrometry (i.e., $\sim 5\%$). In both cases, however, i.e., irradiation at 30°C and -45°C , the amount of product exceeds the estimated G -value for $\text{C}_{15}\text{H}_{31}\cdot$ derived from either acyl or acyloxy dissociation. The amount of pentadecane and other trace products determined for the case of irradiation at 30°C shows a reasonable agreement with the amount of pentadecyl radical precursor. However, the amount of pentadecyl derived components in the case of ethyl palmitate irradiated at -45°C is much greater

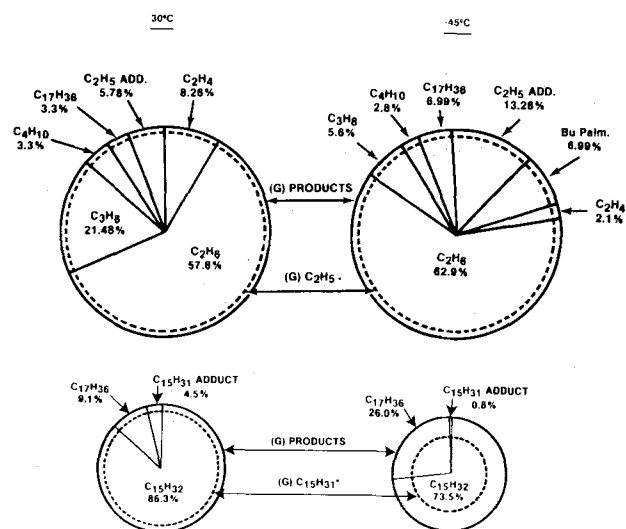
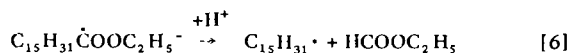


FIG. 6. Diagrams showing the relationship of yields of radiolysis products to their putative precursors. Dashed line, G -value for free radical precursors; solid line, G -value for total derived products — represented as areas of the enclosed circles. Relative contributions of each compound shown as pie sections.

than the estimated G-value for the pentadecyl radical precursor. It is apparent, therefore, that another process must exist by which pentadecyl radical is formed in addition to dissociation of acyl and acyloxy radicals.

The principal mechanism by which ethyl palmitate radical anion formed by electron attachment is dissociated when discharged is presumed to be by formation of palmitic acid and the ethyl radical. A possible alternative pathway for dissociation is by formation of pentadecyl radical and ethyl formate.

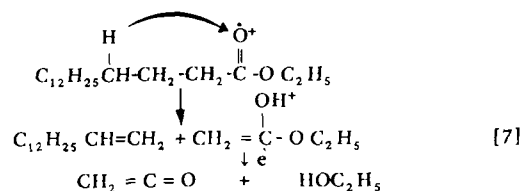


This reaction may account for the pentadecyl radical needed to form the excess pentadecane. Mass spectrometric determination of volatiles in the 30 C sample showed the presence of an amount of ethyl formate corresponding to a G-value of 0.05. This gives a revised value of $G = 0.41$ for pentadecyl radical (vide supra) and a new balance of pentadecyl radical vis à vis pentadecyl derived components ($G = 0.44$). These values show a percent difference of 7.0 and are the values depicted in the piechart in Figure 6.

In the case of the sample irradiated at -45 C the discrepancy is obviously much larger. Since a reliable determination of ethyl formate in the -45 C sample is not available, it is not known at present if a lower temperature favors the dissociation of ethyl palmitate radical anion toward pentadecyl radical and ethyl formate vs palmitic acid and ethyl radical. The excess pentadecane and related derivatives vis à vis postulated pentadecyl radical, however, tends to support the conclusion that more pentadecyl radical is formed than can be attributed to dissociation of acyl and acyloxy radicals.

Several other compounds were observed among the radiolysis products which indicate alternative pathways to the principal routes described above. The formation of butyl palmitate in solid ethyl palmitate has been described previously (vide supra). Corresponding compounds resulting from β cleavage of the ethyl palmitate are tetradecane and ethyl acetate (see Fig. 5). These were found to have G-values of 0.01 and 0.02, respectively. Some of the tetradecyl radicals formed from the cleavage appear among the radiolysis products in the 30 C sample as the adduct, ethyl α -tetradecylpalmitate ($G = 0.02$). A small amount ($G = 0.01$) of ethyl acetate was found among the volatile components of the irradiated solid ethyl palmitate, but no tetradecane or tetradecyl adduct was observed in the corresponding chromatograms.

One of the more abundant radiolysis products is tetradecene, $G = 0.08$ (30 C). This compound cannot be regarded as resulting from disproportionation of tetradecyl free radical, since it is found in substantially greater abundance than tetradecane. Moreover, bimolecular reactions appear not to be favored in the system since recombination products such as octacosane and triacontane are barely detectable. No mechanism for the formation of tetradecene (and related C_{n-2} alkenes among radiolysis products) has been satisfactorily adduced from product analysis or other methods such as ESR, although a McLafferty type rearrangement (analogous to mass spectrometry) of a positive ion intermediate has been postulated (34). Evidence for the fate of the resulting counter ion, however, has not been given. It seems likely, however, that discharge of the counter ion would yield ketene and ethanol.



Although a small amount of ketene was found in this study, the yield could not be determined with sufficient accuracy to verify the postulated mechanism by material balance. The hypothesis that C_{n-2} alkenes are expulsion compounds is supported by the fact that no radiolysis products are found which suggest the existence of an alkenyl free radical in the system. A follow-up study in which the volatile compounds are determined by gas chromatography rather than direct mass spectrometry as employed herein might provide results with the required accuracy to resolve this question.

Most of the mechanisms postulated (vide supra) for the formation of the observed products are supported by the excellent quantitative agreement of the yield obtained with the putative precursors. A final summation of the G-values corresponding to the various reaction pathways is given in Table II.

The principal reaction is clearly electron attachment yielding mainly palmitic acid. Reactions of the corresponding positive ion intermediate are discerned mainly through secondary processes, i.e., formation of the ethyl palmitate radical (by deprotonation) or of an excited state ethyl palmitate (by electron capture). The other significant pathways, therefore, leading to radiolysis products are acyl and

TABLE II
Summary of G-values for Reaction Pathways^{a,b}

Pathway	Transient species	Correlative compound	G-value
Hydrogen atom dissociation	H \cdot	Hydrogen	2.17
Electron attachment	EP \cdot^-	Palmitic acid	0.9
α -abstraction	EP \cdot	Ethyl palmitate adducts	1.54 ^c
Acyl dissociation	RCO \cdot	Ethanol	0.25
Acyloxy dissociation	RCOO \cdot	Carbon dioxide	0.18
Positive ion dissociation	EP $^+$	Tetradecene	0.08
Beta cleavage	R' \cdot	Tetradecane	0.01

^aSee Figure 5.

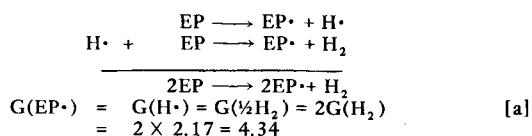
^bData for 30 C.

^c2(EP) $_2$ + EPR.

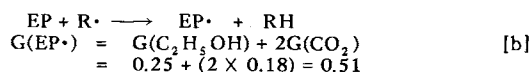
EP = ethyl palmitate; R = C₁₅H₃₁; R' = C₁₄H₂₉.

acyloxy dissociation of the excited state molecule, and adduct formation. The ethyl palmitate radical obtained by hydrogen dissociation, positive ion deprotonation or hydrogen abstraction by other free radicals generated in the system yields a significant amount of adduct compounds by recombination with like radicals (dimerization), or with various alkyl radicals (ethyl α -alkylpalmitates). Only small amounts of products from cleavage or positive ion dissociation are found, and the products of bimolecular reactions such as disproportionation and recombination (except for the predominant ethyl palmitate adduct formation) are of low abundance.

The data, unfortunately, do not account quantitatively for the fate of the ethyl palmitate radical. Considering the relationships involved as follows:



and

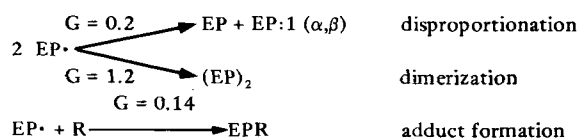


where EP = ethyl palmitate and R = C₂H₅, C₁₅H₃₁ and C₁₅H₃₁CO

$$\therefore \sum \text{G}(\text{EP}\cdot) = 4.85 \quad [\text{a \& b}]$$

(The reader may satisfy himself, since $G = \mu\text{moles/g/Mr}$, that $G(\frac{1}{2}\text{H}_2) = 2\text{G}(\text{H}_2)$ from the identity $\mu\text{g/l} = 2 \mu\text{g}/2$.)

The ethyl palmitate radical is seen to decay by three observed pathways:



where R = C₂H₅, C₁₄H₂₉ and C₁₅H₃₁
 $\sum \text{G}(\text{EP products}) = 1.54$

Although the ethyl palmitate alpha abstraction radical is one of the predominant moieties in the system, only about one third of it can be accounted for by the observed products. Since there are no unidentified compounds among the components separated by GC, it is difficult to speculate on the nature of alternative pathways.

Consideration of the fate of the various transient intermediates (EP]⁺, EP⁻, EP[•], EP*) present in the system suggests that they may react to regenerate ethyl palmitate. ESR studies have shown that the abstraction radical does not increase linearly with dose as do radiolysis products, but rather reaches a steady state concentration above ca. 6 Mrad (J.W. Halliday, private communication). Some speculation has been given to the possibility of the discharge of EP[•] by capture of an electron to form the carbanion followed by protonation to yield ethyl palmitate (I.A. Taub, private communication). It is not possible to elucidate such mechanisms by product analysis, but ESR studies may provide further elucidation of the mechanisms involved.

The overall material balance achieved in this study indi-

cates that all the significant compounds have been identified and that it has been possible to account for the distribution of energy.

ACKNOWLEDGMENT

The authors thank I.A. Taub and J.W. Halliday for many helpful discussions and B.A. Wasilchuk for help with data processing.

REFERENCES

- Merritt, C., Jr., S.R. Bresnick, M.L. Bazinet, J.T. Walsh and P. Angelini, *J. Agric. Food Chem.* 7:784 (1959).
- Merritt, C., Jr., J.T. Walsh, M.L. Bazinet, R.E. Kramer and S.R. Bresnick, *JAOCS* 42:57 (1965).
- Merritt, C., Jr., P. Angelini, M.L. Bazinet and D.J. McAdoo, *Adv. Chem. Ser.* 56:225 (1966).
- Merritt, C., Jr., in *Food Irradiation*, IAEA, Vienna, Austria, 1966, pp. 197-210.
- Merritt, C., Jr., P. Angelini and D.J. McAdoo, *Adv. Chem. Ser.* 65:26 (1967).
- Champagne, J.R., and W.W. Nawar, *J. Food Sci.* 34:335 (1969).
- Merritt, C., Jr., and P. Angelini, *Radiat. Res. Rev.* 3:353 (1972).
- Merritt, C., Jr., P. Angelini, E. Wierbicki and G.W. Shults, *J. Agric. Food Chem.* 23:1037 (1975).
- Merritt, C., Jr., P. Angelini and W.W. Nawar, in *Food Preservation by Irradiation*, Vol. II, IAEA, Vienna, Austria, 1978, pp. 97-112.
- Merritt, C., Jr., P. Angelini and R.A. Graham, *J. Agric. Chem.* 26:29 (1978).
- Vajdi, M., W.W. Nawar and C. Merritt, Jr., *JAOCS* 56:611 (1979).
- Merritt, C., Jr., in *Food Irradiation Information Bulletin No. 10*, International Project in the Field of Food Irradiation, Karlsruhe, German Federal Republic, 1980, pp. 20-23.
- Dubravcic, M.F., and W.W. Nawar, *JAOCS* 45:656 (1968).
- LeTellier, P.R., and W.W. Nawar, *J. Agric. Food Chem.* 20:129 (1972).
- LeTellier, P.R., and W.W. Nawar, *JAOCS* 49:259 (1972).
- Nawar, W.W., *Radiat. Res. Rev.* 3:327 (1972).
- Nawar, W.W., *Prog. Chem. Fats Other Lipids*, Pergamon Press, 13:91 (1972).
- Meidani, J., W.W. Nawar, W.G. Yeomans and C. Merritt, Jr., *JAOCS* 54:496 (1977).
- Nawar, W.W., *J. Agric. Food Chem.* 26:21 (1978).
- Merritt, C., Jr., and M. Vajdi, *JAOCS* 59:172 (1982).
- Vajdi, M., W.W. Nawar and C. Merritt, Jr., *JAOCS* 59:38 (1982).
- Vajdi, M., W.W. Nawar and C. Merritt, Jr., *JAOCS* 55:849 (1978).
- Sheppard, C.W., and V.L. Burton, *J. Am. Chem. Soc.* 68:1636 (1946).
- Luck, H., Q. Nahar Rahman and R. Kohn, *Fette Siefen Anstrichm.* 68:851 (1966).
- Howton, D.R., and G. Wu, *J. Am. Chem. Soc.* 89:516 (1967).
- Angelini, P., D.A. Forss, M.L. Bazinet and C. Merritt, Jr., *JAOCS* 44:26 (1967).
- Merritt, C., Jr., in *Preparative Gas Chromatography*, edited by A. Zlatkis and V. Pretorius, John Wiley and Sons, Inc., New York, 1971, pp. 235-276.
- Merritt, C., Jr., P. Angelini and M. Vajdi, *JAOCS* (scheduled for August).
- Bazinet, M.L., and C. Merritt, Jr., *Anal. Chem.* 34:1143 (1962).
- Ryhage, R., and E. Stenhagen, in *Mass Spectrometry of Organic Ions*, edited by F.W. McLafferty, John Wiley and Sons, Inc., New York, 1963, chap. 9.
- Vajdi, M., W.W. Nawar and C. Merritt, Jr., *JAOCS* 60:978 (1983).
- Budzikiewicz, H., C. Djerassi and D.H. Williams, *Mass Spectrometry of Organic Compounds*, Holden-Day, Inc., San Francisco, 1967, chap. 4.
- Ryhage, R., and E. Stenhagen, *Ark. Kemi* 14:483 (1959).
- Williams, T.F., *Nature* 194:348 (1962).
- Sevilla, M.D., K.M. Morehouse and S. Swarts, *J. Phys. Chem.* 85:923 (1981).

[Received January 6, 1983]