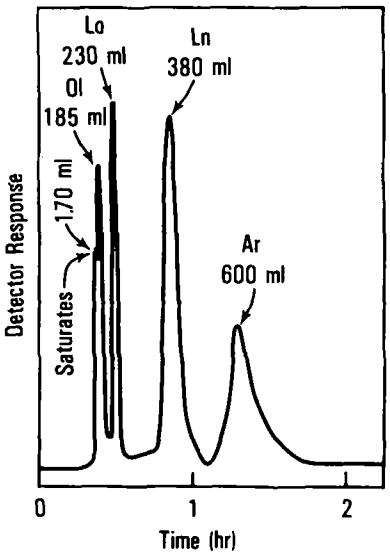

FIG. 6. Separation of: saturates, Ol, Lo, Ln and Ar on column A, 7.2 mL 20% ACN in acetone/min. Sample size 130 mg.

1.5 L of solvent would be needed for reequilibration or ca. 3.5 hr at 7 mL/min. Therefore, it is not convenient to solvent program large columns. No change in the resolution of column B was noted in several months of use. Columns should not be allowed to drain. We found it necessary to repack the large column (A) if air entered the top of the column. The resin was washed out and slurry-packed as described to restore the column.

ACN is a powerful eluent for polyunsaturated esters from fully silver-loaded ion exchange resins in column chromatography. Its use in combination with MeOH or acetone allows separation of methylene-interrupted polyunsaturated esters that are difficult to elute from silver-resin columns. By increasing the proportion of ACN in the solvent according to the degree of unsaturation of the desired component, preparative separations may be effected on one column, which previously would have required the use of a number of partial argentation resin columns (PARC columns [6-8]).

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Identification of Adduct Radiolysis Products from Ethyl Palmitate and Ethyl Oleate

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ABSTRACT

Radiolysis induced adduct products have been separated and identified from irradiated ethyl palmitate, ethyl α-d_2-palmitate and ethyl oleate. In the saturated compounds, adduct formation was observed mainly at the position α to the carbonyl group. The three major adduct products identified in irradiated ethyl palmitate were ethyl α-tetradecylpalmitate, ethyl α-pentadecylpalmitate and the α,α'-dimer of ethyl palmitate. Corresponding compounds were identified from the irradiated ethyl α-deuteropalmitate. Adduct radiolysis products formed in ethyl oleate were identified as the monoene and diene dimers.

INTRODUCTION

Prior studies (1-3, 5) have provided evidence for the formation of radiolysis products of higher molecular weight than that of the starting material. Recently, the adduct compounds formed from tributyrin and tripalmitin have been reported (5). This study is concerned with the identification of the adduct compounds produced by the irradiation of fatty acid esters in order to elucidate the mechanism for their formation. The compounds chosen were ethyl palmitate, ethyl α-deuteropalmitate and ethyl oleate. The selection of these compounds was based on the expectation that the separation and identification of the adduct radiolysis products could be easily performed by gas chromatography-mass spectrometry (GC-MS).

EXPERIMENTAL

The materials used in this study were purchased from Fisher Scientific Co. (Medford, MA); Applied Science Lab., Inc. (State College, PA); ICN Pharmaceuticals, Inc. (Plainview, NY); and Sigma Chemical Co. (St. Louis, MO). The α-deuterated ester was synthesized (6) from the α-deuterated palmitic acid. Purity of each compound examined by GC-

MS analysis (5) was found to exceed 99%.

Analysis of the radiolysis induced adduct products was carried out on 1-g samples of the respective esters irradiated at 25 Mrad at 25 C under vacuum ($\sim 10^{-3}$ Torr).

The irradiated ethyl palmitate, ethyl α-deuteropalmitate and ethyl oleate samples were injected directly into a Perkin-Elmer Model 3920 gas chromatograph fitted with a 4 ft × 1/8 in. column packed with 3% Dexil 400 on Chromasorb W. Liquid chromatograms were obtained on a Waters Associates' liquid chromatographic system using a reversed-phase 1 ft × ½ in. C_{18} Bondapak column with (90:10) methanol/ethyl acetate as the eluent.

GC-MS/computer analysis of the radiolysis products was carried out on a PE Model 3920 gas chromatograph coupled to a DuPont Model 21-491 double-focussing mass spectrometer via a glass jet molecular separator. Mass spectral data were acquired and analyzed by Hewlett-Packard Model 2116 and Digital Equipment Corp. Model PDP 15/76 computers.

A mass spectrum of the separated mixture of ethyl oleate adducts was also acquired by means of a solids insertion probe on a Consolidated Electrodynamics Corporation Model 21-110 mass spectrometer.

RESULTS AND DISCUSSION

Ethyl Palmitate

The gas chromatographic separation of the radiolysis adduct products in irradiated ethyl palmitate is shown in Figure 1A. GC-MS analysis of the sample by electron impact (EI) mass spectrometry revealed three radiolytically induced recombination products indicated by peaks in the chromatogram not seen in the unirradiated control.

The mass spectrum of peak 1 is shown in Figure 2 and is seen to display characteristic ions for an α branched ester. Upon interpretation, the spectrum is found to be that of a mixture of the ethyl esters of α and β branched tetradecylpalmitic acid. The structures, with the indication of appropriate fragmentations, are shown on the figure. The molecular ion is seen at m/e 480. The most abundant ion is the diagnostic McLafferty rearrangement ion (7) for an α-substituted ester seen at m/e 284. Only one such rearrangement ion is found for the α-tetradecyl branched compound since the molecule is symmetrical about the α-position.

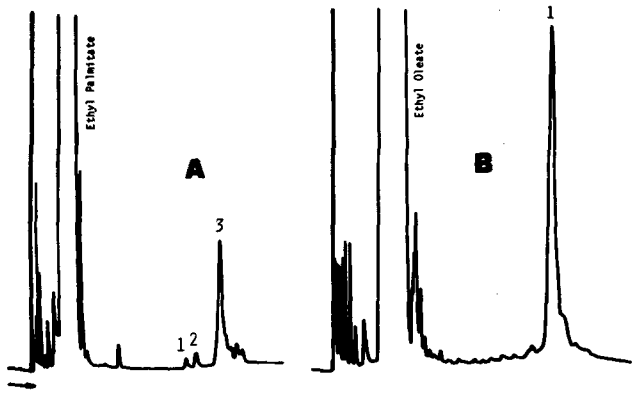


FIG. 1. Gas chromatograms of adduct products from irradiated ethyl palmitate (A) and ethyl oleate (B). Column: 4 ft × 1/8 in. - 3% Dexil 400; temperature: 200-340 C at 8 C/min.; attenuation: 4 × 100; flow rate: 300 mL/min.; sample size: 4 μL.

The occurrence of a β isomer is seen by the appearance of a McLafferty ion at m/e 88, which is typical of non-α-branched ethyl esters, and fragment ions at m/e 283 and 297 corresponding to the branched alkyl chains.

Although it is difficult to determine accurately the relative amounts of the two isomers, observation of the relative abundances of m/e 88 *vis à vis* m/e 284 (base peaks in the respective normalized spectra of the individual components) in the composite spectrum shows that the α isomer is present in greater amount.

The composite mass spectrum obtained for peak 2 in the gas chromatogram showed the presence of two molecular ions at m/e 450 and 494. Characteristic ions were observed at m/e 88, 239, 255, 284, and 298.

Deconvolution of the composite spectrum by means of selected ion vs scan number plots showed that an individual spectrum for each of the compounds could be obtained by choice of an appropriate scan number. The resulting spectra of the individual components are shown in Figure 3. The compound whose spectrum is shown in scan number 36 (Fig. 3A) has been identified as palmitone (di-*n*-pentadecyl ketone). The spectrum is found to conform to the previously published spectrum of authentic palmitone (4).

The formation of palmitone has been observed previously in irradiated palmitic acid (2) and in irradiated beef (3).

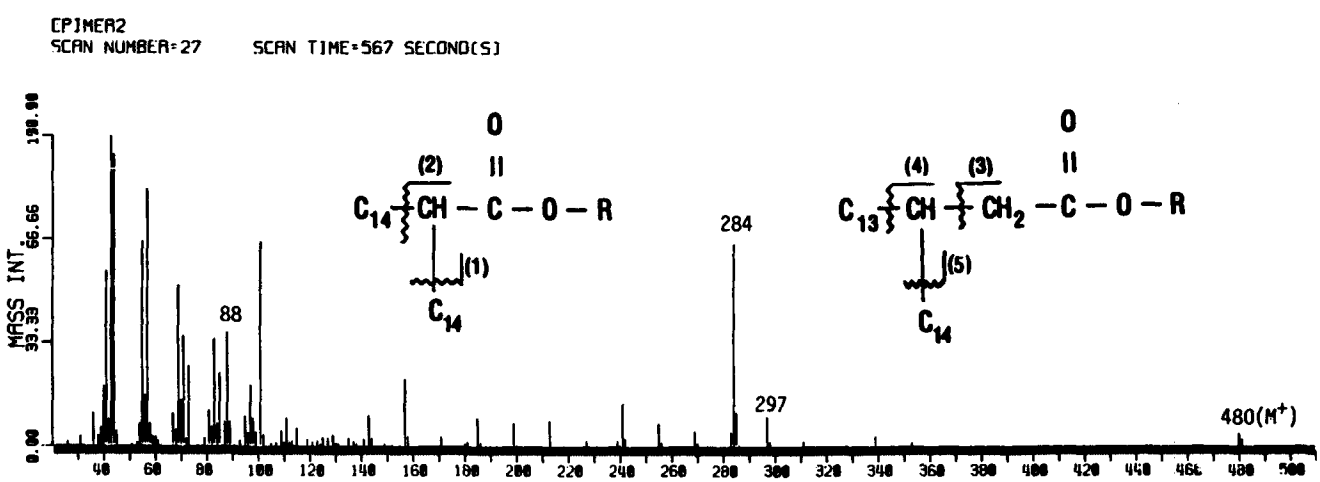


FIG. 2. Composite mass spectrum of the components of peak 1, Figure 1A.

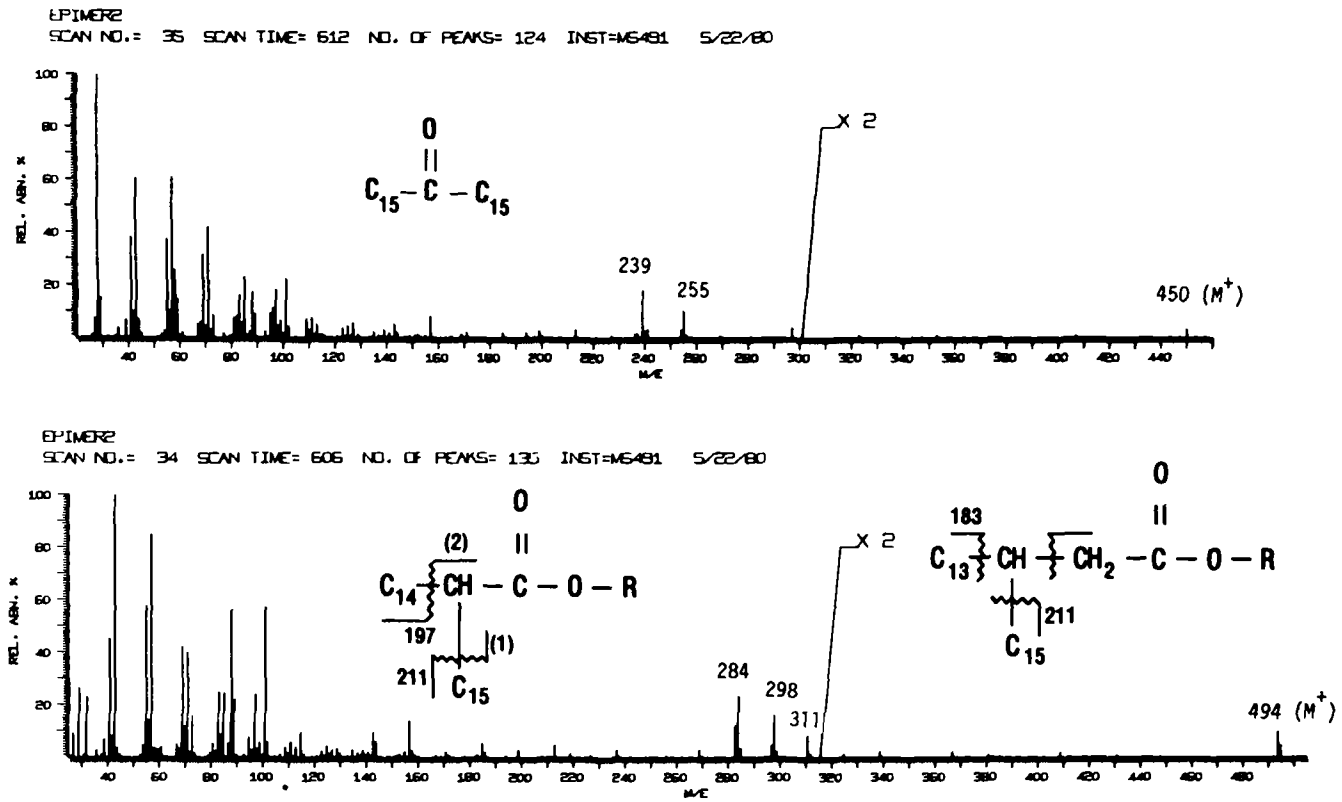


FIG. 3. Deconvolated mass spectra of the components of peak 2, Figure 1A.

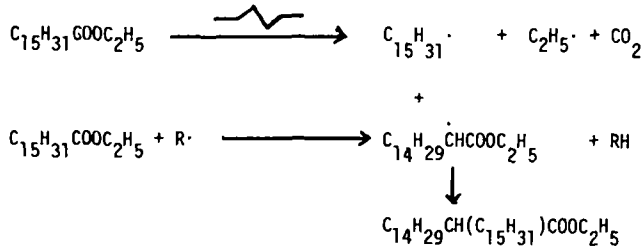
A mechanism for its formation has been given (8).

The compound corresponding to mass spectrum scan number 34 as shown in Figure 3B was identified as ethyl α-pentadecylpalmitate. Mass peaks at m/e 284 and 298 represent McLafferty rearrangement ions produced by a transfer of a hydrogen atom to the carbonyl group and cleavages at sites 1 and 2 (Fig. 3B) with the loss of C_{15} and C_{14} alkenes, respectively.

The mass spectrum of Figure 3B suggests that the β isomer is also present as seen by the occurrence of a McLafferty ion at m/e 88 and by M-183 (m/e 311) and M-211 (m/e 283) ions.

A mechanism for the formation of alkyl adducts (e.g., pentadecyl) in irradiated esters may be depicted as in Scheme 1. α-Alkyl adduct formation has been shown also to be characteristic of radiolytic adducts in triglycerides (5).

Mass spectral analysis of peak no. 3 in Figure 1A shows the presence of a dehydrodimer of ethyl palmitate, M = 566



SCHEME 1

(Fig. 4). Characteristic ions at m/e 283 (M/2) and 284 (M/2 + 1) correspond to cleavage of the bond joining the tertiary carbon atoms of the two monomers (9). An ion at m/e 238 corresponds to the same cleavage with the simultaneous loss of an ethoxy group (M/2 - C_2H_5O). Similarly, ions at m/e 237 and 236 correspond to loss of C_2H_5OH and $C_2H_5OH_2$ fragments, respectively, from M/2. The two typical frag-

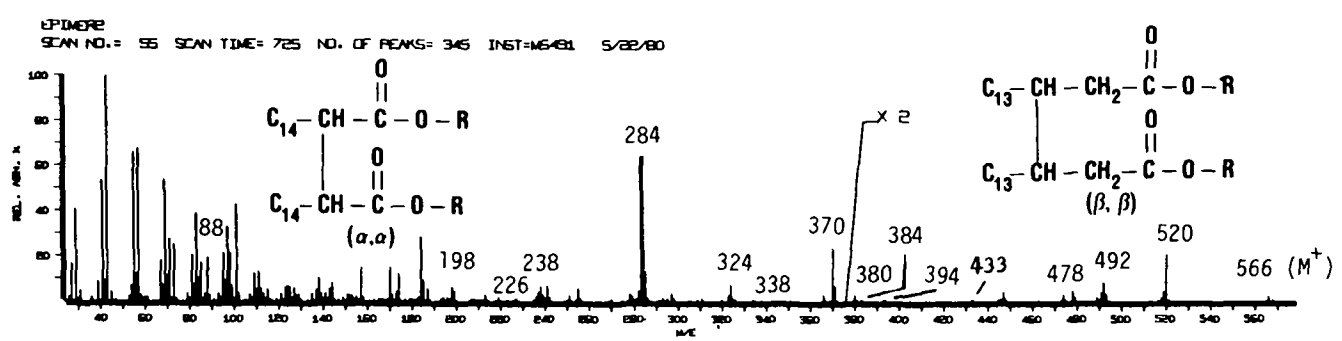
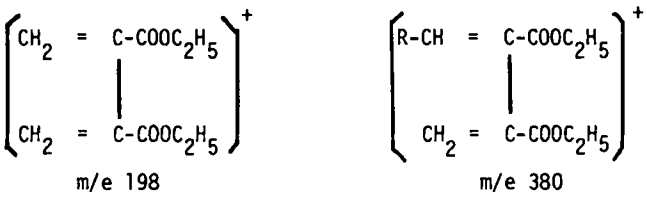


FIG. 4. Composite mass spectrum of the components of peak 3, Figure 1A.

mentations representative of α-crosslinking arise from the loss of an alkyl group adjacent to the linkage and by similar cleavage with the additional loss of an ethoxy group to yield ions at m/e 370 [M-($C_{14}H_{29}$ - 1)] and 324 [M-($C_{14}H_{29}$ + C_2H_5O)]. Ions at m/e 520 and 492 arise from loss of C_2H_5OH (M-46) and C_2H_5COOH (M-74) from the molecule. Other characteristic ions were seen at m/e 198 and 380. These ions are depicted in Scheme 2. Analogous ions were observed in the spectrum of methyl stearate dimer (9).

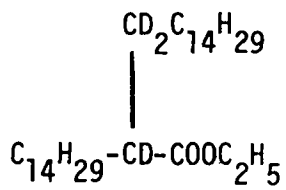


SCHEME 2

The presence of an ion at mass 88 due to the McLafferty ion ($CH_2COOC_2H_5$ + H) is typical of non-α-substituted esters and suggests the presence of an isomeric adduct. A weak ion at m/e 478 corresponding to the loss of the McLafferty rearrangement ion from the molecule is also observed. Although it is not known whether ions analogous to those seen at 198 and 380 for an α,α′ linked dimer are formed at other positions, ions which could correspond to a β,β′ adduct are seen at very low abundance at m/e 226 and 394. Other ions related to the β,β′ configuration are given in Table I. Addition at the β,β′ position seems to be the likely structure for the isomeric dimer. Based on the relative abundance of selected fragmentation ions, viz. m/e 88 and 284 the α,α′ adduct is the major component of the two isomeric structures (Fig. 4).

Deuterated Ethyl Palmitate

The direct GC-MS analysis of ethyl α-d_2-palmitate was similar to that of the nondeuterated compound. The mass spectra from this sample indicated that GC peak 1 (Fig. 1A) corresponded to a tetradecyl adduct with a mass increase of one and that GC peak 2 was composed of a deuterated palmitone and ethyl (α-d_2-pentadecyl) α-d_1-palmitate (Scheme 3).



SCHEME 3

The typical fragmentation of detuerated palmitone revealed mass peaks at m/e 241 (α-cleavage) and 259 (β-cleavage with double hydrogen rearrangement). These ions are 2 and 4 amu greater than the corresponding ions in the undeuterated compound. Similarly, for the ethyl (α-d_2-pentadecyl)α-d_1-palmitate mass peaks at m/e 285 and m/e 301 corresponding to losses of $C_{15}D_2H_{29}$ and $C_{14}H_{29}$ were observed.

Mass spectral analysis of peak 3 representing the dimer products in the gas chromatogram of irradiated ethyl α-

TABLE I

Summary of Fragment Loss Ions Observed in the Spectra of Ethyl Palmitate Dimers

Fragment Loss	Mass	Figure 4 αα M =	Figure 4 αα M/2 =	Figure 4 ββ M =	Figure 4 ββ M/2 =	Figure 5 αα(d_2) M =	Figure 5 αα(d_2) M/2 =	Figure 5 ββ(d_4) M =	Figure 5 ββ(d_4) M/2 =	Figure 5 αβ(d_3) M =	Figure 5 αβ(d_3) M/2 =
C_2H_5O	45	**521**	238	**521**	238	**523**	239	525	240	**524**	239, 240
C_2H_5OH	46	520	237	520	237	522	238	524	239	**523**	238, 239
$C_2H_5OH_2$	47		236		236		237		238		237, 238
C_2H_5COOH	74	492		492		494		496		**495**	
$CH_2COOC_2H_5$	87			**479**							
$CD_2COOC_2H_5$	89							481		480	
$2C_2H_5O$	90	*476*		476		478		480		479	
$CH_2COOC_2H_5 + C_2H_5OH$	133			433							
$CD_2COOC_2H_5 + C_2H_5O$	134							436		435	
$CD_2COOC_2H_5 + C_2H_5OH$	135							435		*434*	
$(C_{12}H_{25} + 1) + 2H$	172			**394**				*398*			
$(C_{13}H_{27} + 1) + 2H$	186	380				*382*					
$C_{13}H_{26}$	182			**384**				*388*		387	
$C_{14}H_{28}$	196	370				372				**373**	
$C_{13}H_{27} + C_2H_5O$	228			**338**				*342*		341	
$C_{14}H_{28} + C_2H_5O$	242					**326**				327	
$2(C_{12}H_{25}) + 2H$	340			226				*230*			
$2(C_{13}H_{27}) + 2H$	368	198				200					

Bold face: less than 1% relative abundance; italics: not observed.

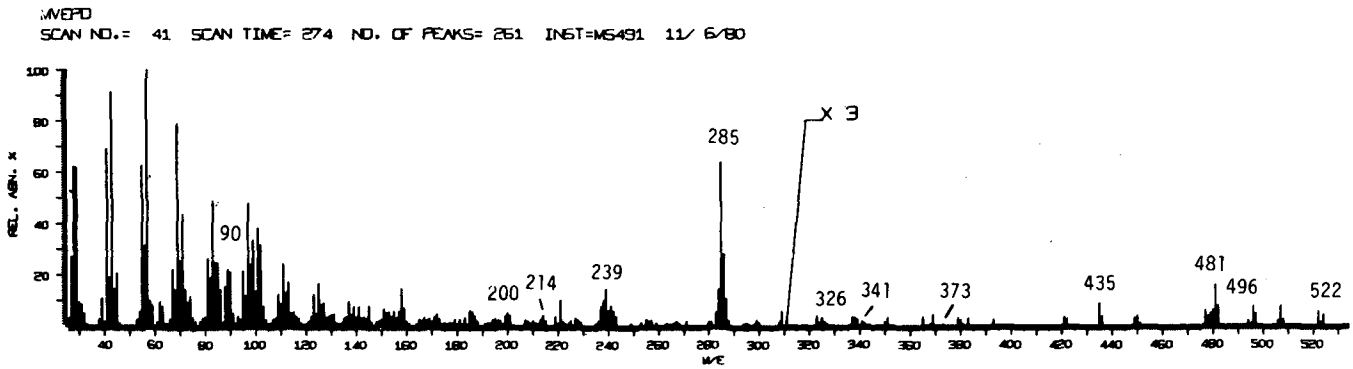
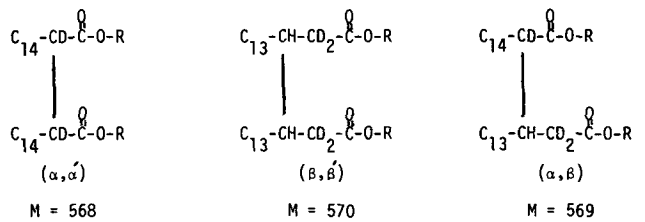


FIG. 5. Composite mass spectrum of the components corresponding to peak 3, Figure 1A from irradiated ethyl α-d_2-palmitate.

deuteropalmitate revealed the presence of at least three isomeric forms. The composite spectrum is shown in Figure 5. As a result of deuterium labeling at the α carbon in the parent compound and the observation of labeled ions in the product, structures corresponding to dimer adduct formation at the α-α′, β-β′, and α-β sites are postulated in Scheme 4.



SCHEME 4

The molecular ions are unfortunately not observed. The mass peaks corresponding to the spectrum of an α-α′ dimer (MW 568) showed cleavage of the bond joining the two chains by the occurrence of a characteristic ion at m/e 284 (M/2). Ions at m/e 239, 238, 237 are related to the same cleavage with simultaneous loss of C_2H_5O, C_2H_5OH, and C_2H_5OH + H from M/2 fragment. Ions at m/e 522 (M-C_2H_5OH), 523 (M-C_2H_5O) and 478 (M-2C_2H_5O) expected of an ester of a dibasic acid (10) were likewise seen in the spectrum. The occurrence of relatively strong peaks at m/e 283 and 285 (M/2 ± 1) due to hydrogen rearrangement (9-11) was also observed, as were other ions corresponding to M-74 (m/e 494) and [M-($C_{14}H_{29}$ + C_2H_5O)] (m/e 326). The mass of all the ions corresponded to an appropriate increase for the deuterated moieties when compared with the spectrum of undeuterated ethyl palmitate dimer (see Table I).

Ions relating to the β-β′ dimer (MW = 570) are observed in the spectrum at m/e 285 (M/2), and at m/e 240, 239, and 238 corresponding to losses of C_2H_5O, C_2H_5OH, and C_2H_5OH + H from the M/2 fragment. Losses of fragments C_2H_5OH, and 2(C_2H_5O) from the molecular ion giving rise to peaks at m/e 524 and 480 are seen as well. Other peaks at m/e 496 and 342 corresponding to M-74 and [M-($C_{13}H_{27}$ + C_2H_5O)] are present. The occurrence of a peak at m/e 90 (McLafferty ion) confirmed the β-addition.

A very small mass peak at m/e 523 (569-46) suggests the presence of an α-β configuration (probably not due to 568-45, since M-45 is not abundant in the spectrum of the undeuterated α-α′ dimer.) Most of the other ions arising from fragmentation of an α-β dimer have the same mass as those of the α-α′ and β-β′ forms, but unique ions at m/e 327 [M-($C_{14}H_{29}$ + C_2H_5O)], 341 [M-($C_{13}H_{27}$ + C_2H_5OH)] and 373 (M-$C_{14}H_{28}$) indicate a trace amount of the α-β dimer may be formed.

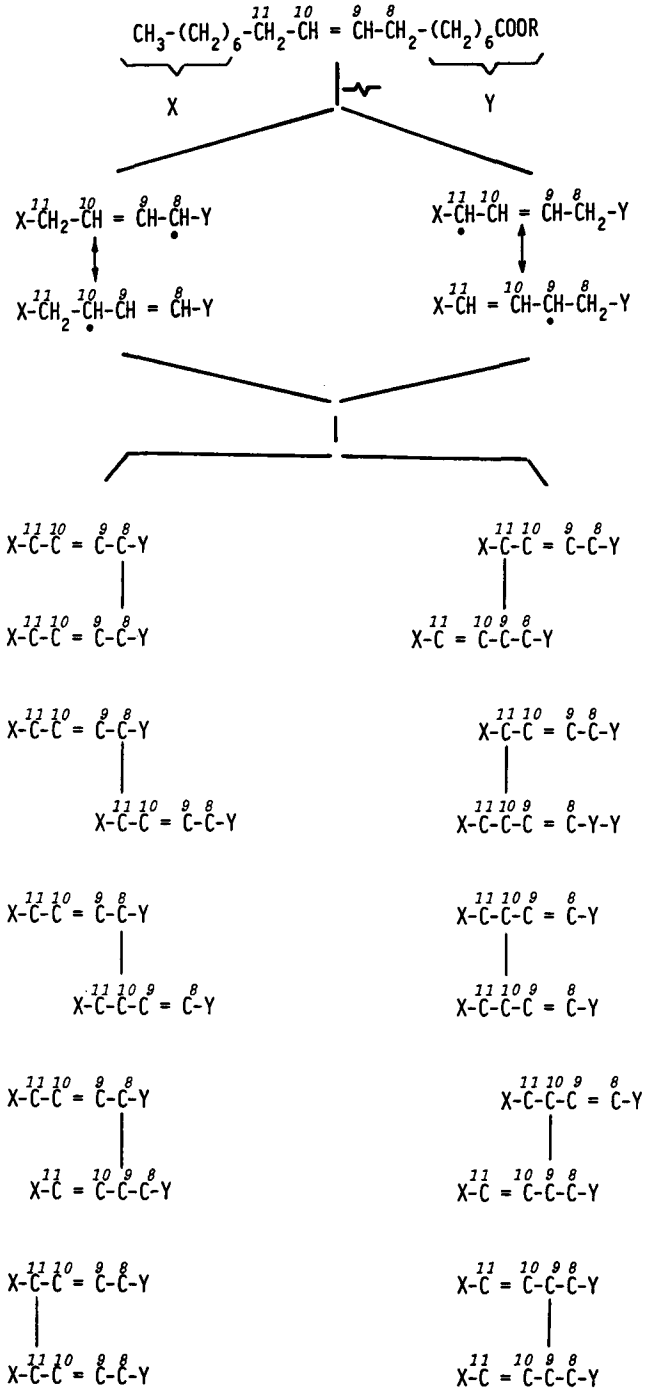
Ethyl Oleate

The use of various catalysts to form dimer products of unsaturated fatty acids has been described in several studies (9-11,14,15). Adduct compounds are formed also by heat and irradiation. It has been postulated that such dimer products formed by various means (Lewis acids, clay, di-*t*-butyl peroxide, heat and irradiation) are somewhat different in structure (14,15). In an irradiated oleic acid ester, one would expect to observe the formation of a variety of adduct radiolysis products induced by a free radical mechanism. Since the formation of a free radical is equally likely at carbons 8, 9, 10, and 11, one would expect to observe the formation of 10 possible isomers (10) (Scheme 5). The bond joining the two oleate fragments is between two tertiary carbons and is allylic to two double bonds. This feature is common to all the isomeric forms and results in completely isometric (i.e., having the same mass) fragment ions, vide infra, in the composite mass spectrum (Fig. 6).

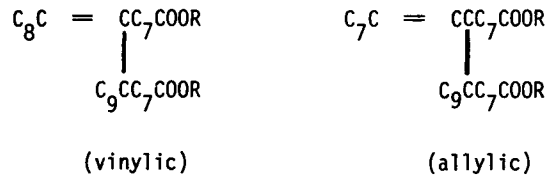
In addition to the diene dimers formed by a free radical mechanism, other studies (12,13) have indicated the presence of one double bond in the adduct products postulated to be formed through an ionic pathway. It is believed (13) that the ionic process may lead to either vinylic or allylic branching (crosslinking at or adjacent to the double bond), as shown in Scheme 6.

Howton et al. (13), however, suggested further that resonance stabilized allylic free radical intermediates would be expected to attain relatively high steady-state concentrations, favoring eventual reaction by coupling with a second radical of the same type to form diene dimers. The presence of five- and six-member rings in thermally treated methyl oleate (11) and clay-catalyzed oleic acid dimer (15) has been also suggested. This study was undertaken to ascertain the nature of the crosslinking in irradiation induced dimers of ethyl oleate.

A gas chromatogram of irradiated ethyl oleate showed the presence of one major peak corresponding to the adduct radiolysis products (Fig. 1B). A liquid chromatogram (Fig. 7) was obtained, which also showed the presence of a single long retention peak corresponding to the adducts. Mass spectral analysis of peak 1 in the gas chromatogram revealed



SCHEME 5



SCHEME 6

the presence of two types of structure (Fig. 6). The presence of dimer adducts corresponding to the possible configurations outlined in Schemes 5 and 6 may be deduced from consideration of the ions observed in the spectrum.

The structure for the dimers having double unsaturation (Scheme 5) would give rise to a molecular ion at m/e 618 which is observed in the spectrum. Other ions corresponding to cleavage of the dimer bond are seen at m/e 309 (M/2) and m/e 308 (M/2-1). Loss of hydrogen from the half molecular ion has been previously reported (11) for the mass spectrum of the methyl oleate doubly unsaturated dimer. Ions corresponding to the loss of alcohol moieties from the molecular ion and the half molecular ion, as likewise reported previously for the methyl oleate doubly unsaturated dimer, are seen also in the ethyl oleate dimer spectrum obtained in this study. These ions are summarized in Table II. Thus, abundant ions at m/e 573 and 572 corresponding to losses of C_2H_5O and C_2H_5OH fragments, respectively, from the molecular ion were observed in the spectrum, as well as other ions corresponding to losses of C_2H_5O, C_2H_5OH, and C_2H_5OH + H from the half molecular ion seen at m/e 264, 263, and 262.

The preferential loss of alkane fragments (C_7 and C_8) is expected, since these are the only fragments attached to a tertiary carbon which is also allylic. Ions corresponding to these fragments are seen at m/e 519 and 505, respectively. Similar fragments were observed due to the loss of the ester chain from the molecular ion giving rise to peaks at m/e 461 (M-$C_6H_{12}COOC_2H_5$) and 447 (M-$C_7H_{14}COOC_2H_5$). Ions derived from the loss of fragments corresponding to the hydrocarbon moiety with a double bond (see Scheme 5) are expected to be observed as alkenyl ions, since the charge in such a cleavage would be retained on the unsaturated fragment. These ions are indeed observed at m/e 125 and 139. The analogous ions corresponding to a moiety having both unsaturation and the ester group are not observed, but this is also expected since such ions are unstable and would undergo further fragmentation. The ions thus formed constitute many of the ions seen in the low mass region of the spectrum. All the ions observed in the spectrum are consis-

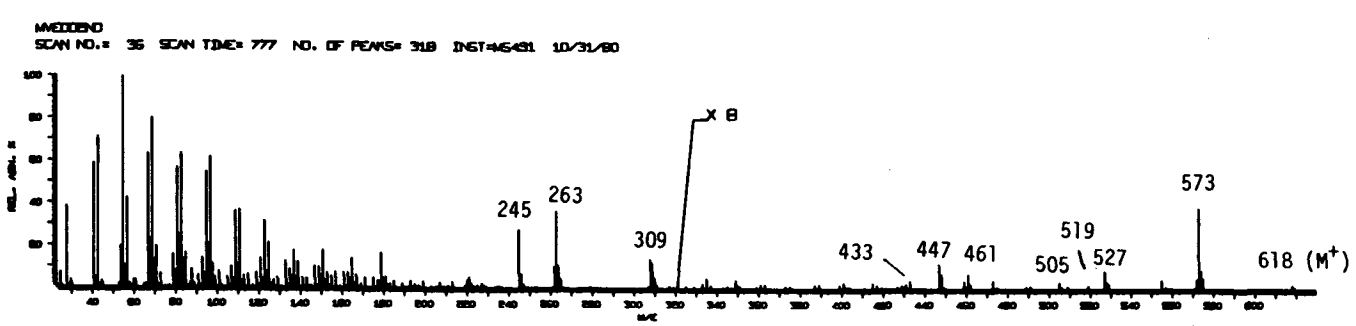


FIG. 6. Composite mass spectrum of the components of peak 1, Figure 1B.

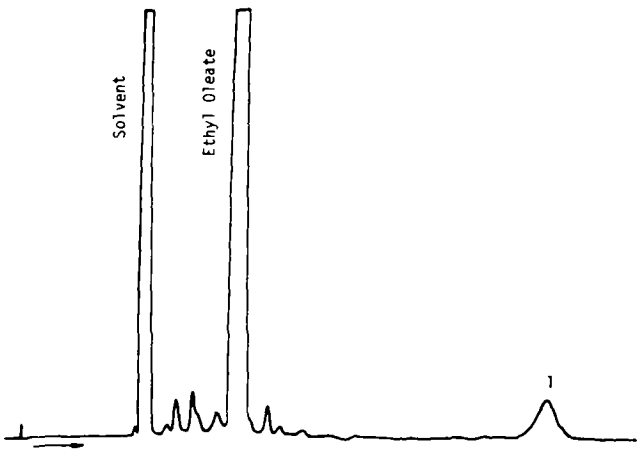


FIG. 7. Liquid chromatogram of the adduct products from irradiated ethyl oleate. Column: C_{18} Bondapak (Waters Associates); solvent: 10% ethyl acetate/methanol; flow rate: 2 mL/min.; attenuation 16 X (RI); sample size: 15 μL.

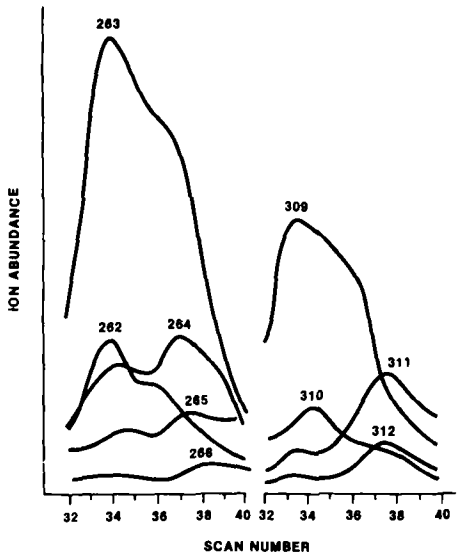


FIG. 8. Plot of the relative intensities of selected ions as a function of mass spectrum scan number for chromatographic peak no. 1 shown in Figure 1B. (See Table III for description of selected ions.)

tent with those expected for a doubly unsaturated dimer of ethyl oleate. All the fragment ions predicted and observed are common to each of the 10 isomers. It is, therefore, impossible to distinguish them.

The shoulder seen on both gas and liquid chromatograms is shown below by mass spectrometric deconvolution to be due to the presence of a lesser amount of the monoene dimer.

Evidence for a monounsaturated dimer is not readily deduced from the spectrum in Figure 6. The molecular ion, m/e 620, is not observed in the spectrum, and the half molecular ion, m/e 311, has a low abundance. Likewise, ions corresponding to the loss of alkyl groups (i.e., M-C_7, M-C_8, etc.) are not abundant (see Table II). Ions possibly related to cleavages of alcohol moieties from the molecular ion or half molecular ion are, in general, isometric with such ions derived from the doubly unsaturated dimers or have such low abundance that their presence may be attributed to isotopic homologs. A significantly unique ion of this type, (M/2 - C_2H_5O, m/e 266) was not observed.

The spectrum shown in Figure 6 is taken at the apex of peak 1 of the gas chromatogram (MS scan no. 36). The

TABLE II

Summary of Fragment Loss Ions Observed in the Spectra of Ethyl Oleate Dimers

Fragment loss	Mass	Diene dimers		Monoene dimers	
		M = 618	M/2 = 309[a]	M = 620	M/2 = 311
C_3H_7	43	575		*577*	
C_2H_5O	45	573	264	575[b]	266
C_2H_5OH	46	572	263	574	265
$C_2H_5OH_2$	47	571	262	573[b]	264[b]
$C_2H_5O + C_2H_5OH$	91	527		529	
$2C_2H_5OH$	92	**526**		528	
C_7H_{15}	99	519		**521**	
C_8H_{17}	113	505		**507**	
C_9H_{19}	127	491		*493*	
$C_7H_{15} + C_2H_5OH$	145	**473**		475	
$C_8H_{17} + C_2H_5OH$	159	**459**		461[b]	
$C_9H_{19} + C_2H_5OH$	173	**445**		447[b]	
$C_{10}H_{21} + C_2H_5OH$	187	431		433[b]	
$(CH_2)_6COOC_2H_5$	157	461		**463**	
$(CH_2)_7COOC_2H_5$	171	447		**449**	
$(CH_2)_8COOC_2H_5$	185	433		**435**	
$(CH_2)_9COOC_2H_5$	199	419		**421**	
$C_7H_{15} + 2(C_2H_5OH)$	191	**427**		429	
$C_8H_{17} + 2(C_2H_5OH)$	205	**413**		415	
$C_9H_{19} + 2(C_2H_5OH)$	219	399		401[b]	
$C_{10}H_{21} + 2(C_2H_5OH)$	233	*385*		387[b]	
$C_7H_{15}COOC_2H_5 + C_2H_5OH$	217	401		403	
$C_8H_{17}COOC_2H_5 + C_2H_5OH$	231	387		389	
$C_9H_{19}COOC_2H_5 + C_2H_5OH$	245	373		375	
$C_{10}H_{21}COOC_2H_5 + C_2H_5OH$	291	359		361	

[a]Also a fragment of M = 620.

[b]Isometric ions of 618 and 620.

Bold face: less than 1% relative abundance; italics: not observed.

TABLE III

Summary of Characteristic Ions Displayed in Figure 8

Ion type	Diene	Monoene[b]
M/2	309[a]	311
M/2 + 1	310	312
M/2 - C_2H_5O	264	266
M/2 - C_2H_5OH	263[a]	265
M/2 - $C_2H_5OH_2$	262	264

[a]One half of monoene dimer gives ions isomeric with those of the diene dimer.

[b]Ions derived from saturated half of the dimer.

shoulder on the chromatogram indicates the presence ot another partially resolved component. Accordingly, a series of selected ion chromatograms was constructed over the spectrum scan range of interest. In order to enhance the appearance of ions of very low abundance, the intensities are plotted as the percent of total ionization rather than normalized to the most abundant peak as in Figure 6. The graph is shown in Figure 8 for the ions associated with the half mass and the corresponding fragment losses of alcohol moieties. The characteristic ions are summarized in Table III. Thus, ions associated with the diene dimers, (viz. m/e 262, 263, 264, 309 and 310), are seen to show a maximum abundance in scan number 34. Significantly, m/e 266 is now observed as a unique ion for the monoene dimer in scan number 38.

An analogous argument based on a consideration of a postulated structure for a cyclic dimer, its expected fragmentation pattern, and the observed ions in the spectrum failed to provide conclusive evidence for its presence.

To enhance the spectrum and obtain an estimate of the relative amounts of the diene and monoene species, a fraction containing the adducts as a mixture was collected from the LC separation, the solvent evaporated, and a spectrum obtained by means of direct solids analysis (Fig. 9). The molecular ions for both types of dimer are clearly seen, as are the ions at half mass. The series of ions corresponding to the various fragment losses are seen mainly for the diene dimers. The unique peak for the monoene at 266 is seen to have a very low abundance. Although a monoene dimer is undoubtedly formed, the main course of adduct formation leads to the diene isomers.

The possibility of α,α' crosslinking was also considered. However, no ions attributable to such a structure were found.

From this study it is concluded that radiation yields mainly an α,α' crossed linked dimer in ethyl palmitate and isomeric doubly unsaturated dimers cross linked at positions 8, 9, 10, and 11 in ethyl oleate.

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M.L. Bazinet acquired the mass spectrum of the mixed dimers of ethyl oleate by direct solids analysis,and D.M. Alabran synthesized ethyl α-deuteropalmitate.

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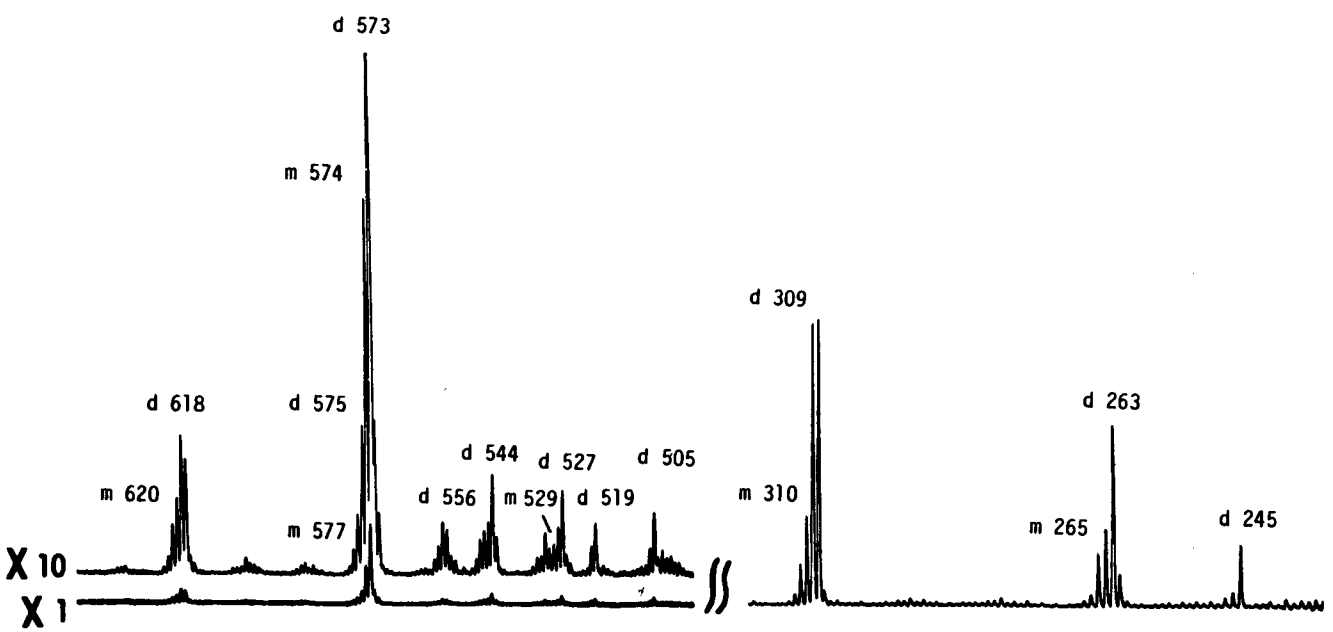

FIG. 9. Composite mass spectrum of the collected components from the liquid chromatographic separation of the adduct products from irradiated ethyl oleate (see Fig. 7). Masses attributable to dimer species; d = diene, m = monoene.

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Supplementation of Bakery Items with High Protein Peanut Flour

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ABSTRACT

White skin peanuts were defatted with hexane to produce flours with 55-60% protein. The peanut flour was used to replace 12.5% of the wheat flour in bread, 100% of wheat flour in muffins, and 10, 15 or 50% of the wheat flour in cookies. At 12.5% levels of peanut flour, total solids, protein, moisture retention of bread after baking, and dietary fiber contents are increased without affecting loaf volume. Crust color of supplemented bakery items is darker brown, texture is coarse for bread and harder in cookies, but not enough to make them unacceptable. Peanut flour muffins with a net protein content of 33-40% can serve as a high protein snack food or bakery item, possibly for patients with celiac disease who cannot tolerate wheat flour. Moisture retention in supplemented products was greater than in nonsupplemented controls. Net increase of protein in baked items varied from 4% increase for 12.5% peanut flour bread to 30% for the all-peanut flour muffins. Other physical and chemical properties of these products are presented to support potential applications of peanut flour as a supplement for selected food products.

INTRODUCTION

Oilseed proteins are expected to play an increasing role in meeting the world's future needs for edible protein to replace decreasing or economically inaccessible supplies of animal protein, if they can be formulated into foods that look and taste like traditional foods. Fortifying bread with legume or oilseed proteins is one of the primary methods available for raising protein levels in human diets for economic and/or health reasons. Proper food and water are two of the most basic needs of all people, but religious, cultural and social habits frequently govern their eating habits. Even in today's affluent societies, there is a growing interest in "back to nature" or "natural" type foods in which dark breads or specialty breads are something of a status symbol, more so than the traditional wheat breads that have been enriched with vitamins and minerals for several decades (1). Four ounces of a protein-fortified bread can provide 20% of the US recommended daily allowance of protein for adults (2). For this reason there has been a great increase in research on the fortification of wheat bread with various types of protein, such as single cell protein (3), cottonseed, soybean, peanut and sunflower proteins (4,5), lentil, sunflower, faba bean, field pea and soy proteins (6-9), cowpea powder (10), potato protein (11), safflower protein (12), Great Northern Bean proteins (13), and fish protein concentrate and green algae (14). High protein flours and meals from red skin peanuts have been used in breads (4,5,15,16) but, unless the skins are removed before oil extraction, a flour darker than wheat flour is produced, which then yields darker bread color in fortified loaves (15).

Bread is not the only bakery item being fortified with oilseed and legume proteins. Because of a growing desire to raise the nutritional level of snack foods, various kinds of cookies (17-20), biscuits (21), and corn muffins (22) have been fortified with oilseed or legume proteins but none of these reports tested all-oilseed flour baked products, possibly because of the lower volume and heavier texture of such products compared to wheat flour products. Ranhotra et al. (20) and McWatters (19) reported that fortification of cookies with nutritionally significant levels of nonwheat proteins adversely affected their quality and acceptability. However, modification of formulation and processing technologies with flavors and dough conditioners improved product quality. To offset the adverse effects of soy flour on cookie spread while maintaining high levels of soy protein for its nutritional value, Ranhotra (23) substantially increased the level of shortening in the formula.

Bread is an ideal food for protein fortification since it is a major staple throughout the world, and peanuts can serve as a source of protein for fortification since they are already accepted as human food. Several years ago, studies were begun at the Southern Regional Research Center (SRRC) on white skin peanuts that did not have the typical peanut flavor/aroma after roasting, did not have to be blanched before oil removal (resulting in lower processing costs), produced a white high protein flour, had little or no flatus-causing sugars, and had a protein profile similar to red skin varieties (24,25). Defatted white skin peanut flour appears to be an ideal source of bland, white flour that should be comparable to other oilseed/legume proteins for fortification of baked goods. Data are presented on the chemical characteristics of two white skin peanut flours used in protein fortification of bread, cookies and muffins.

EXPERIMENTAL

The two varieties of white skin peanuts, PI288160 (SR57) and Spanwhite (C32W), were grown in experimental plots in Tifton, GA. After harvesting, drying, shelling and sorting, the seeds were shipped to the SRRC, New Orleans, LA, where they were flaked, deoiled by hexane solvent-extraction, dried, desolventized, and ground to a fine flour in the Engineering and Development Laboratory. Samples of the