peaks but can be counted as major peaks (intensity, 10-95%). The fragments produced from McLafferty rearrangement and γ cleavage are shown in Figure 2 (refer to Table II). The strong characteristic peak at m/e 57 (78%) in compound IV is due to the stable *tert*-butylcarbonium ion (Grubb and Meyerson, 1963).

NMR Spectra. NMR spectra of 11 alkylpyrazines and their interpretations are shown in Figure 1. Compounds I, II, and III show very similar fragmentation patterns in their mass spectra. These can easily be distinguished from each other by using NMR spectra of their alkyl substitutes. Compound I shows a typical long aliphatic chain [δ 0.85 (3 H, t, $-CH_3$), 1.15-1.45 (4 H, m, $-CH_2-CH_2-$), 1.45-1.85 (2 H, m, $-CH_2-$)]. Compound II shows a terminal isopropyl group [δ 0.95 [6 H, d, $-CH(CH_3)_2$], 1.3-1.8 [3 H, m, $-CH$-$(CH_3)_2$ and $-CH_2-CH(CH_3)_2$]]. Compound III exhibits neither of these.

The pyrazines can generally be identified by mass spectra alone on the basis of their typical fragmentation patterns. Sometimes, however, it is difficult to identify the structure of side chains by MS alone. In these cases, NMR spectra can be used to confirm the structure of the side chains. The hydrogen atoms on an α-carbon (a carbon atom next to the pyrazine ring) are deshielded to δ 2.5. The chemical shifts of the other hydrogens on the alkyl groups are the same as those of the individual hydrocarbons except for the methyl groups on the α-carbon, which are deshielded to δ 1.23 (compounds V, VI, and X).

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Influence of Polyunsaturation on Thermal Decomposition of Saturated Triacylglycerols

The typical oxidative products of saturated triacylglycerols could not be detected when heated in the presence of ethyl linoleate. The qualitative patterns of the volatiles produced from the heated mixtures were essentially the same as those obtained from the unsaturated ester when heated alone. The major products typical of the autoxidation of saturated tyiacylglycersols were practically absent. However, the relative amounts of specific decomposition products of linoleate autoxidation were altered when heated in the presence of saturated triacylglycerols.

Frying fats as well as food lipids undergo chemical decomposition when food is exposed to heat in the presence of oxygen. Such reactions are responsible for both desirable and undesirable changes in the flavor and nutritional quality of food. A great deal of information is available regarding the oxidative reactions of pure saturated and unsaturated fatty acid systems. However, the effect of the presence of one substrate fatty acid on the oxidative decomposition of another is not clear. Only one study could be found in which the volatile oxidation products from mixtures of specific triacylglycerols were investigated (Selke et al., 1980). Samples containing triolein and trilinolein produced volatiles which could be ascribed to each substrate. On the other hand, heated mixtures of tristearin-trilinolein produced no observable volatiles that could be related to the saturated triglyceride.

The present work was undertaken to study the influence of heat on saturated and unsaturated fats when coexisting in the same reaction medium. Model systems consisting of unsaturated ethyl esters and saturated triacylglycerols were used.

EXPERIMENTAL SECTION

Tricaproin, trilaurin, trimyristin, and ethyl linoleate were purchased commercially and purified by cold finger distillation as described previously (Nawar et al., 1969). One-gram samples of the saturated triacylglycerol alone or the unsaturated ethyl esters alone or mixtures containing 1 g of each were heated in 250-mL round-bottom flasks fitted with ground glass stoppers at 180 °C for 1 h. The methods used for separation and identification of the decomposition products were the same as those previously reported (Crnjar et al., 1980).

RESULTS AND DISCUSSION

Gas chromatographic analyses of heated trilaurin, ethyl linoleate, and the trilaurin-ethyl linoleate mixture are

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Table I. Relative Amounts (Percent)[a] of Thermal Oxidation Products from Linoleate and Linoleate–Triacylglycerol Mixtures

peak no. in Figure 1	compd	Et-18:2	Et-18:2 + Tri-6	Et-18:2 + Tri-12	Et-18:2 + Tri-14
15	hexanal	22.01	15.12	13.85	19.22
16	ethyl hexanoate[b]				
17	2-heptenal	16.46	12.90	17.74	19.32
18	ethyl octanoate	21.88	23.80	21.64	21.14
20	trans,cis-2,4-decadienal	1.94	3.92	6.08	3.87
21	trans,trans-2,4-decadienal	7.56	17.93	15.72	11.54
22	ethyl 8-oxooctanoate	8.34	11.24	10.77	10.56
23	ethyl 9-oxononanoate	21.83	15.10	14.20	14.35

[a] GC peak areas normalized. [b] Not included in the relative amount (percent) calculation.
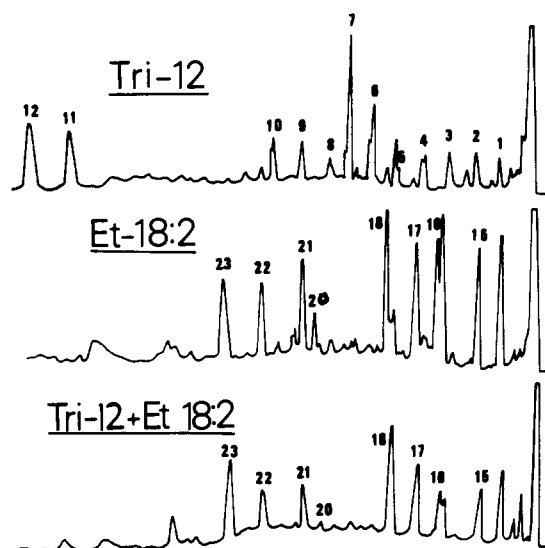

Figure 1. Thermal oxidation of saturated–unsaturated mixtures. (Top curve) Trilaurin alone: peaks 1–7, 2-alkanones C_5–C_{11}; peaks 8–10, γ-lactones C_6–C_8; peaks 11 and 12, γ- and δ-dodecalactones. (Middle and bottom curves) Ethyl linoleate and the mixture, respectively; peak numbers correspond to the compounds in Table I.

shown in Figure 1.   The major oxidative products of heated ethyl linoleate and ethyl linoleate–triacylglycerol mixtures are listed in Table I.   Relative peak areas after normalization are given for only those compounds expected from primary cleavage of linoleate hydroperoxides. Thermal oxidation products of trilaurin included the methyl ketone series C_5 to C_{11} with the 2-undecanone being the most abundant, a γ-lactone series of which the C_{12} compound was produced in relatively large quantity, and one δ-lactone of an equal number of carbon atoms to the substrate fatty acid (Figure 1, top trace). This is consistent with oxidative patterns of saturated fatty acid systems as observed by several investigators (Crnjar et al., 1980; Crossley et al., 1962; Endres et al., 1962; Kleinau and Neitzel, 1970; Selke et al., 1975).

The major products obtained from ethyl linoleate when heated alone (Table I and the middle curve in Figure 1) were essentially those expected from classic linoleate autoxidation as observed by others (Chan et al., 1976; Chang et al., 1978; Frankel et al., 1977; Henderson et al., 1980; Selke et al, 1977; Swoboda and Lea, 1965).

When trilaurin was heated in the presence of ethyl linoleate, the thermal oxidative products typical of trilaurin autoxidation could not be detected. The volatile pattern of the mixture was essentially the same as that of ethyl linoleate (Figure 1). The same phenomenon, i.e., the disappearance of oxidative products of the saturated acids when dienes are present, was also obtained when linoleate

was heated with either tricaproin or trimyristin. The unsaturated acids thus appear to inhibit the autoxidation of the saturated chains. This suggests that alkoxy radicals, rather than attacking methylene groups of a saturated chain, are more likely to abstract hydrogen preferentially from the pentadiene system of linoleate. Thus, a competitive oxidative effect when substrates of different reactivity are present could be involved, as previously discussed by Mayo (1968). The presence of unsaturation, however, does not appear to have a significant influence on nonoxidative reactions of the saturated system. When linoleate esters were present with tricaproin during heating, decomposition products included the symmetric ketone and diol diesters (Crnjar et al., 1980), but γ- and δ-hexalactones were absent.

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