Studies on the Thermal Degradation of Naturally Occurring Materials. II. Products from the Pyrolysis of Triglycerides at 400°

Elizabeth Barr Higman,* Irwin Schmeltz,[1] Howard C. Higman, and Orestes T. Chortyk

Tripalmitin, tristearin, and soybean oil were selected as model triglycerides for pyrolysis. Pyrolyses were conducted at 400° under nitrogen. Products generated were identified using combined gas chromatography-mass spectrometry. In addition, some acids were individually isolated as their methyl esters by preparative gas chromatography and were identified by high-resolution mass spectrometry. Pyrolyzates produced fell into two general categories, hydrocarbons and carboxylic acids. Homologous series of alkanes, alkenes, saturated and mono-unsaturated carboxylic acids, and dicarboxylic acids were formed.

During the course of our studies designed to establish precursor-product relationships between components of tobacco smoke and compounds present in the tobacco leaf, we have reported the pyrolytic behavior of proteins, amino acids, carbohydrates, and fatty materials at relatively high temperatures; *i.e.*, above 800° [since the maximum temperature in the cigarette cone has been found to be 880° (Stedman, 1968)]. At such temperatures, as a rule, these substances generate polynuclear aromatic hydrocarbons and other characteristic products containing aromatic rings (Chortyk *et al.*, 1966; Halaby and Fagerson, 1970; Higman *et al.*, 1970).

Since a sharp temperature gradient occurs in a narrow region behind the burning cone of a cigarette, it appeared reasonable to extend our studies to lower temperatures. We therefore exposed long-chain hydrocarbons, stearic acid, and other related compounds to pyrolyses at 650 and 450° (Schlotzhauer *et al.*, 1970). It was found that dotriacontane, a representative compound, gave rise to a homologous series of monoolefins at 650°, while at the lower temperature it merely distilled. Similar results were obtained with stearic acid and other relatively long-chain compounds (Schlotzhauer *et al.*, 1970).

Turning our attention to more complex systems, we concerned ourselves with the pyrolysis of triglycerides, the results of which are reported herein. Studies of this kind are not new, inasmuch as earlier workers have studied the pyrolysis of tricaprin (Crossley *et al.*, 1962), 2-oleo-dipalmitin (Crossley *et al.*, 1962), trilaurin (Kitamura, 1971), and tripalmitin (Kitamura, 1971). Extending these studies, we pyrolyzed tristearin and soybean oil, and repeated the pyrolysis of tripalmitin using, among other methodology, combined gas chromatography-mass spectrometry (gc-ms) to characterize the products thus formed. As will be noted below, our experimental conditions varied from those of earlier workers. Therefore, as might be expected, some of the products we report were either not generated or overlooked in previous work, while other products were identical to those reported by the earlier workers cited above.

The results of these studies should be of interest, not only to the tobacco industry but also to the food industry, since the compounds discussed are also abundant in foodstuffs. Consequently, the thermal reactions reported may also occur in foods during cooking or processing.

EXPERIMENTAL SECTION

Materials. Tristearin and tripalmitin (Eastman Organic Chemicals, Rochester, N. Y.) with a purity of >95% were used as obtained. Soybean oil (cooperative sample from Northern Regional Research Laboratory, USDA, alkali bleached and refined) was used as obtained.

Pyrolyses. Pyrolyses were performed in a Vycor tube (2.6 cm o.d. × 35 cm length) positioned horizontally inside a Lindberg Hevi-Duty Furnace maintained at 400 ± 10°. A Chromel-Alumel thermocouple was used to monitor pyrolysis temperature, and the pyrolysis tube was flushed continuously with nitrogen.

Samples in 1- to 3-g quantities were loaded into ceramic boats which were placed inside the preheated Vycor tube prior to pyrolysis. Condensable products were collected in a series of three traps, the first cooled in ice-water, and the second and third cooled in Dry Ice-acetone. The remaining product stream then passed through a gas scrubber containing diethyl ether and 5% aqueous NaOH.

Fractionation of Pyrolyzate. The pyrolyzate was washed out of the traps (and tube) with diethyl ether and 5% aqueous sodium hydroxide, successively. The two washings were combined with the corresponding solutions from the gas scrubber, and the combined solutions were then mutually extracted, yielding an ether solution containing neutrals and an aqueous solution containing acids (as salts). The neutral fraction "B" in ether was dried over anhydrous sodium sulfate and concentrated. The pH of the aqueous solution was adjusted to pH 1.5 with 25% aqueous sulfuric acid. The resulting acidified solution was washed with ether; the ether washings (containing acids) were then combined, dried, and concentrated to yield acid fraction "A."

For the triglycerides, the above procedure yielded a precipitate "C," usually formed when alkali was added to the pyrolyzate. This precipitate was thought to be the sodium salt of a long-chained acid. In the case of tristearin, a small amount of precipitate was dissolved in aqueous acid, washed with ether, dried, and esterified. The acid was identified by ir spectra, and gc analysis of the resulting ester indicated that stearic acid accounted for 98% of the organic portion of C.

Methylation of Acids. The dried ether solution of acids (fraction A) was methylated with diazomethane prepared from Diazald by the conventional method. The diazomethane in ether was added until the presence of an excess was indicated by the persistence of a yellow color. The reaction mixture was allowed to stand for 1 hr, during which time excess diazomethane evaporated.

Gas Chromatographic Analysis. Gc analysis of both ether solutions (hydrocarbons and methyl esters) was generally performed on a Varian Aerograph Model 200 gas chromatograph equipped with dual stainless steel columns

(10 ft × 0.25 in o.d.) packed with 20% SE-52 on 60/80 mesh Chromosorb W. Column temperature was programmed ·from 70 to 250° at 8°/min. Detector and injector temperatures were set at 275°, and helium flow was set at 75 ml/min.

Additional gc analyses were performed on a Varian Aerograph Model 2700 under conditions similar to those noted above, except that a 20% SE-30 column on Chromosorb W (6 ft × 0.25 in. o.d.) was used. Also, the helium flow rate was 35 ml/min, and the injector temperature was 250°.

Combined Gas Chromatography–Mass Spectrometry (gc-ms). Initially neutral fraction B (hydrocarbons) was examined by combined gc-ms on a Varian Model 1740 flame ionization gas chromatograph equipped with a 1:1 effluent splitter in tandem with a DuPont 21-492 mass spectrometer. Gc detector and injector temperatures were 250 and 200°, respectively. The gc column (10 ft × 0.125 in. o.d. stainless steel packed with 20% SE-30 on 60/80 mesh, acid-washed Chromosorb W) was programmed from 60 to 180° at 6°/min. Helium flow was 35 ml/min.

Subsequently, both the neutral and acid (as methyl esters) fractions were examined by combined gc-ms using a Varian Aerograph 1400 single column flame ionization instrument equipped with a 1:1 effluent splitter in conjunction with a DuPont 21-492 mass spectrometer. In this case, the gc column (5 ft × 0.125 in. o.d. stainless steel packed with 6% SE-30 on 100/120 mesh Varopart 30) was programmed from 50 to 200° at 6°/min; helium flow was 35 ml/min. Detector and injector temperatures were 250 and 210°, respectively.

Mass Spectrometry. In some cases individual methyl esters (unknowns) were collected as they eluted from the exit port of the Varian Aerograph 200 gas chromatograph and analyzed by mass spectrometry on a CEC-110 instrument.

Qualitative and Quantitative Determinations. In general, acids were characterized on the basis of the gas chromatographic retention data of their methyl esters and the mass spectra of selected effluents collected from the gas chromatograph. In addition, the acids generated from tripalmitin were identified by combined gc-ms of their methyl esters. Hydrocarbons were also characterized by combined gc-ms, which revealed the dual nature of each gc peak; i.e., a mixture of alkane and alkene of the same carbon number. Generally, chromatographic peaks for alkene-alkane mixtures are expressed in the tables as alkanes. Relative yields of pyrolytic products were determined by measuring the corresponding peak areas on gas chromatograms by the method of triangulation.

RESULTS AND DISCUSSION

Pyrolytic conditions and some residue yields from the pyrolyses (soybean oil, tripalmitin, tristearin) are given in Table I. Duration of each pyrolysis was relatively long, with thermal degradation of the triglycerides occurring rather slowly. Thus, overall reproducibility of conditions may have been difficult to attain, leading to the variation in yields noted. From the data, it appears that the neu-

Table I. Pyrolytic Conditions and Some Overall Yields

Material pyrolyzed	Quantity, g	Pyrolysis[a] duration. hr	Residue weights, g		
			Neutrals (B)	Acids (A)	Carbon[b]
Soybean oil	0.8755	5.5	0.1692	0.0164	0.1230
	3.85	5.0	1.320	0.1880	
Tripalmitin	1.011	4.0	0.3845	0.0841[c]	
Tristearin	2.1270	5.5	0.8491	0.1573[d]	0.0115

[a] Conducted at 400°. [b] Left in pyrolysis boat. [c] Additional 0.3200 g of palmitic acid as precipitate C. [d] Additional 0.8562 g of stearic acid as precipitate C.

Table II. Products from Pyrolysis of Tristearin (% Distribution)

Acids[a] (fraction A)		Hydrocarbons[b] (fraction B)	
Propionic	0.52	Heptane	0.27
Butyric	0.56	Octane	0.93
Valeric	1.20	Nonane	0.91
Oxalic	2.45	Decane	1.80
Hexanoic	2.62	Undecane	1.97
Heptanoic	4.15	Dodecane	3.12
Succinic	3.24	Tridecane	3.45
Octanoic	14.43	Tetradecane	4.38
Nonanoic	5.71	Pentadecane	10.26
Decanoic	4.97	Hexadecane	19.44
Undecanoic	2.91	Heptadecane	35.70
Dodecanoic ⎫		Unidentified	17.74
Nonanedioic ⎭	18.61		
Tridecanoic	1.91		
Heptadecanoic	4.90		
Octadecanoic	30.77		
Unidentified	1.20		

[a] In order of increasing gc retention times of corresponding methyl esters. [b] All compounds are mixtures of alkene–alkane; listed in order of increasing gc retention times.

trals constitute a large portion of the pyrolyzate, consistent with earlier studies (Higman et al., 1970). For tripalmitin and tristearin, the single major acidic products were palmitic and stearic acid, respectively. These acids predominantly precipitated out in the fractionation procedure as the alkali salts, as noted before.

In spite of the variations in relative yields, the individual products obtained from each of the triglycerides pyrolyzed showed considerable qualitative similarities, consisting of alkane, alkene, and carboxylic acid homologs. The percent distribution of products in the pyrolysis fractions for tristearin is given in Table II. Similar data for tripalmitin and soybean oil are given in Tables III and IV, respectively. The results for each pyrolyzed substance will be discussed in terms of the major products, namely hydrocarbons and acids.

Hydrocarbons. Hydrocarbons generated by tristearin were observed by gc-ms to consist of C_7 to C_{17} alkanes and alkenes, and at least seven other compounds not identified. Single gas chromatographic peaks were found by gc-ms to be composed of mixtures of alkanes and alkenes of the same carbon number. The peaks corresponding

Table III. Products from Pyrolysis of Tripalmitin (% Distribution)

Acids[a] (fraction A)		Hydrocarbons[c] (fraction B)	
Butyric	0.43	Heptane	0.16
Pentenoic	0.15	Octane	1.81
Pentanoic	6.42	Nonene	1.62
Hexenoic	1.07	Nonane	1.30
Hexanoic	0.69	Decene	3.12
Heptanoic[b]	1.25	Decane	1.54
Octanoic[b]	1.65	Undecane	3.55
Nonanoic[b]	1.81	Dodecane	4.07
Decanoic[b]	2.09	Tridecane	4.45
Undecanoic[b]	2.02	Tetradecane	11.77
Dodecanoic[b]	1.90	Pentadecane	16.78
Tridecanoic[b]	1.13	Hexadecane	25.79
Tetradecanoic[b]	1.92	Heptadecane	2.04
Pentadecanoic	0.38	Octadecane	4.66
Hexadecanoic	73.59	Palmitic acid	2.27
Heptadecanoic	0.14	Heneicosane	2.66
Octadecanoic	1.23	Unknown A[d]	6.48
Unidentified	2.10	Unknown B[e]	5.88

[a] As methyl esters; in order of gc elution time. [b] Mixtures of saturated and monounsaturated acids. [c] In order of gc elution time; hydrocarbons are mixtures of alkane and alkene where only alkane is listed. [d] Molecular weight, 270. [e] Molecular weight, 294.

Table IV. Products from Pyrolysis of Soybean Oil (% Distribution)

Acids[a] (fraction A)			Hydrocarbons[f] (fraction B)	
Propanoic	0.94[b]	0.32[c]	Hexane	5.08
Butyric	2.60	0.51	Heptane	7.49
Valeric	2.34	0.65	Octane	5.02
Hexanoic	4.70	1.38	Nonane	3.20
Heptanoic	19.71	7.40	Decane	2.63
Octanoic	8.15	3.25	Undecane	6.97
Nonanoic	3.94	3.04	Dodecane	3.60
Decanoic	7.99	11.07	Tridecane	4.69
Undecanoic	0.68	1.18	Tetradecane	17.49
Octanedioic	0.57	0.28	Pentadecane	5.26
Dodecanoic		0.60	Hexadecane	6.28
Nonanedioic	2.10	0.54	Heptadecane	7.20
Tridecanoic		0.38	Unidentified	25.04
Dodecanedioic	12.44	3.05		
Tetradecanoic	0.26	0.36		
Undecanedioic	1.53	0.22		
Pentadecanoic	0.54	1.06		
Dodecanedioic	0.86			
Hexadecanoic	8.69[d]	19.33[e]		
Heptadecanoic		0.52		
Octadecanoic	20.37[d]	41.71[e]		
Hexadecanedioic	0.31	0.09		
Eicosanoic	0.31	0.82		
Unidentified	0.96	3.33		

[a] In order of increasing gc retention times of corresponding methyl esters. [b] 400°, N$_2$, 5.5 hr (pyrolysis conditions). [c] 400°, N$_2$, 5 hr (pyrolysis conditions). [d] Plus impurities. [e] Mixture of saturated and unsaturated acids. [f] All hydrocarbons are alkane–alkene mixtures, in order of elution from gc.

to C$_{17}$, C$_{16}$, and C$_{15}$ alkane–alkene mixtures accounted for 36, 19, and 10% of the total gas chromatographic hydrocarbons, respectively (Table II). Ms results indicated the presence of monounsaturated hydrocarbons, but the position of the double bond could not be determined from the data. Based on previous experience and theoretical considerations, α olefins are indicated (Schlotzhauer et al., 1970).

Tripalmitin yielded a series of alkanes and alkenes extending from C$_7$ to C$_{21}$ compounds. Palmitic acid and two compounds with molecular weights of 270 and 294 were also detected. Among the hydrocarbons from tripalmitin, the C$_{16}$ alkane–alkene mixture predominated (26%); C$_{15}$ and C$_{14}$ comprised 17 and 12% of the fraction, respectively, and all other components were in concentrations of 6% and lower.

Soybean oil was observed to generate hydrocarbons similar to the above. They included C$_6$ to C$_{17}$ alkanes–alkenes, and other uncharacterized products in varying amounts. The C$_{14}$ alkane–alkene mixture was the major product, consisting of 17% of the total (Table IV).

The formation of an homologous series of alkanes, although consistent throughout our work, has not been reported by earlier workers. However, the formation of an homologous series of alkenes is consistent with the work of Kitamura (1971). When tripalmitin and trilaurin were pyrolyzed, α olefins were detected in the pyrolysis products. These, Kitamura postulated, were generated by an acid anhydride intermediate formed in the thermal degradation of the triglycerides. Polynuclear aromatic hydrocarbons and phenols were absent from the pyrolyzate, as expected, due to the low pyrolysis temperature (Lam, 1957). Optimum temperature for the formation of polynuclear aromatic hydrocarbons has been found to be 850° (Stedman, 1968), while optimum temperature range for the formation of phenolic material is 500–600° (Schlotzhauer et al., 1967).

Acids. Acids generated by the pyrolysis of triglycerides included alkanoic, alkanedioic, and alkenoic acids. Tri-

stearin, for example, give rise to alkanoic (C$_3$ to C$_{13}$, C$_{17}$, C$_{18}$) and alkanedioic (C$_2$, C$_4$, C$_9$) acids. Stearic acid, a mixture of dodecanoic and nonanedioic acids, and octanoic acid accounted for the major portion of the acidic products (Table II).

Tripalmitin yielded alkanoic acids (C$_4$ to C$_{18}$) and alkenoic acids (C$_5$ to C$_{14}$). Palmitic acid was the major decomposition product (Table III). The acid product in next highest distribution was valeric acid. No evidence for the formation of dicarboxylic acids in the tripalmitin pyrolyzate was found. Dicarboxylic acids were found, however, both in the tristearin and soybean oil pyrolyzates. One might then speculate that the mechanistic pathway to the "unusual" alkenoic acids could involve further thermal degradation of a dicarboxylic acid intermediate via decarboxylation–dehydration to form alkenoic acids. The type of acid formed might merely be a function of residence time or pyrolytic conditions.

Soybean oil was shown to generate C$_3$ to C$_{18}$ and C$_{20}$ alkanoic acids and C$_8$ to C$_{12}$ (and possibly C$_{16}$) alkanedioic acids (Table IV). Here C$_{18}$ acids were generated in greatest concentration in the product mixture (20 and 42% in the two experiments), as might be expected considering the large known concentration of C$_{18}$ acids in soybean oil. It is entirely possible that the stearic acid generated, presumably by cleavage of the ester moiety and simple distillation, may contain unsaturated material. The procedure used for identification of the acids from the tristearin and soybean oil pyrolyzate (co-gas chromatography on an SE-52 column) would not be expected to separate unsaturated and saturated compounds. Other acids produced in relatively high concentrations were heptanoic (20%), decarelatively high concentrations were heptanoic (20%), decanedioic (12%), hexadecanoic (9%), octanoic (8%) and dec-(19%), decanoic (11%), heptanoic (7%), and octanoic, nonanoic, and decanedioic (3% each) in the second experiment. Again, variations in the results of the two experiments probably reflect differences in pyrolytic conditions (Tables I and IV).

Both Crossley's (1962) and Kitamura's (1971) pyrolyses of triglycerides, although performed under different experimental conditions, yielded fatty acids as products. Crossley, in addition to finding alkanoic acids, also found evidence of alkanedioic acids. However, both previous researchers found ketones as pyrolyses products. We identified no ketones. In view of all the products observed in our pyrolyses and those of others, it is extremely difficult to postulate a pyrolytic pathway that will be general or unifying and applicable to all cases. Obviously, processes like decarboxylation, dehydrogenation, dehydration, cracking, and possibly condensation of fragments occur at various points in the pathway, but the questions "Where?" and "Why?" remain open to much speculation.

LITERATURE CITED

Chortyk, O. T., Schlotzhauer, W. S., Stedman, R. L., Beitr. Tabakforsch. 3, 422 (1966).
Crossley, A., Heyes, T. D., Hudson, B. J. F., J. Amer. Oil Chem. Soc. 39, 9 (1962).
Halaby, G. S., Fagerson, I. S., Food Sci. Technol. Proc. Int. Congr. 3rd 820 (1970).
Higman, E. B., Schmeltz, I., Schlotzhauer, W. S., J. Agr. Food Chem. 18, 636 (1970).
Kitamura, K., Bull. Chem. Soc. Jap. 44, 1606 (1971).
Lam, J., Acta. Pathol. Microbiol. Scand. 39, 207 (1957).
Schlotzhauer, W. S., Schmeltz, I., Hickey, L. C., Tobacco Sci. 11, 31 (1967).
Schlotzhauer, W. S., Schmeltz, I., Osman, S. F., Chem. Ind. 1377 (1970).
Stedman, R. L., Chem. Rev. 68, 153 (1968).