Effects of Ionizing Radiation on Some Vegetable Fats

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Abstract

The volatile compounds produced by irradiation, under vacuum at 6 megarads, in five vegetable fats were analyzed qualitatively and quantitatively by gas chromatography and mass spectrometry. A series of compounds, *n*-alkanes, 1-alkenes, internally unsaturated alkenes, alkadienes, alkatrienes, alkanals and methyl and ethyl esters of fatty acids, were identified in each of the fats studied. A wide variation occurs in the amounts of the volatiles produced from each fat. The major radiolytic products were few in number and were found to depend largely on the fatty acid composition of the fat. These compounds were essentially the hydrocarbons containing one or two carbon atoms less than the component fatty acids. This relationship was found consistent if radiolytic products of fats with different fatty acid compositions are compared or if the fatty acid composition of the same fat is altered by hydrogenation. The results correlate well with those of earlier studies on simple triglycerides.

Introduction

As a part of an overall project designed to study the effects of high-energy radiation on lipids, the radiolytic decomposition of some vegetable fats was investigated. A survey of literature showed that very little information is available on this subject. Astrack et al. (1) irradiated cottonseed, castor and linseed oils at 1.5 megarads and found only minor changes in peroxide value, iodine value, acid value, Kreis test and viscosity. Luck and Kohn (6) studied irradiation-induced isomerization in soybean, peanut and olive oil. Only in samples receiving very high doses, 100 megarads, were they able to detect significant changes. Chipault et al. (4) observed odor and flavor changes in corn oil when irradiated in air or in vacuum. These did not correlate with peroxide or carbonyl values. In further studies Chipault and Mizuno (3) found that stability to oxidation in corn oil was considerably reduced by irradiation, but a gradual recovery in stability took place when stored under vacuum.

The availability at the present time of the more sensitive analytical tools such as gas chromatography and mass spectrometry, provided an opportunity to study in some detail a wide range of irradiation-induced products. Recently, Dubravcic and Nawar (5) investigated the radiolysis of several model systems of triglycerides. On the basis of quantitative data, they speculated that while a series of hydrocarbons may be produced in small quantities by random splitting of carbon-carbon bonds along the fatty acid chains, the principal cleavages of glyceride molecules occurred in the vicinity of the carbonyl group. This preferential splitting gives rise to relatively large amounts of hydrocarbons containing one and two carbon atoms less than the glyceride fatty acid and in addition, some oxygen containing compounds of the same carbon numbers as the fatty acid.

In the present study, the products formed by irradiation in safflower, soybean, coconut, corn and olive oil, were analyzed qualitatively and quantitatively. In order to further elucidate the relationship between fatty acid composition and the radiolytic pattern, irradiation of the same fats after partial hydrogenation was also studied.

Experimental Procedures

Materials

Corn oil, safflower oil and olive oil were purchased locally. Coconut oil and soybean oil were obtained through the courtesy of the Procter and Gamble Company, Long Island, N.Y.

Analysis of Fatty Acids

Samples of oil were refluxed with dry 10% hydrochloric acid methanol and the methyl esters analyzed by gas chromatography. A previously calibrated 12 ft × 1/8 in. diethylene glycol succinate column was used in a F&M model 810 flame ionization gas chromatograph.

Hydrogenation

Portions of each oil were partially hydrogenated in a Brown micro-hydrogenator (Delmar Scientific Laboratories, Inc., Maywood, Ill.). The unit uses sodium borohydride to generate both hydrogen and catalyst (2). Since a variety of fatty acid compositions were desired, the degree of hydrogenation was random and no effort was made to reach any specific iodine value.

Irradiation

Ten milliliter samples, sealed under vacuum in 25 ml ampoules, were exposed to gamma rays from the Co^{60} source at the U.S. Army Laboratories at Natick, Mass. All samples received a dose of 6 megarads at 25 C. After irradiation the ampoules were surrounded with dry ice and returned to the laboratory for immediate analysis.

Analysis of Radiolytic Products

Techniques for the qualitative and quantitative analysis of the products of radiolysis have been previously described in detail (7). Essentially the volatiles are separated from the fat by high-vacuum cold-finger distillation. The various components present in the distillate are identified with the aid of a combination gas chromatograph-mass spectrometer system. Quantitative determinations depend on relating GLC peak areas of the identified compounds to that of an appropriate internal standard. For the purpose of this study, only compounds with chain length higher than C_8 were measured.

Results and Discussion

The fatty acid composition as well as the iodine values of the unhydrogenated and hydrogenated fats used for irradiation, are shown in Table I. It can be seen that different degrees of hydrogenation were achieved in the various fats, resulting in a variety of samples with varied fatty acid composition. Fatty acid analysis before and after irradiation showed that

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TABLE I
Fatty Acid Composition of Unhydrogenated and Partially Hydrogenated Fats Used For Irradiation (%)

	Safflower		Soybean		Coconut		Corn		Olive	
Carbon number	Unhyd. I.V. 144	Hyd. I.V. 1	Unhyd. I.V. 127	Hyd. I.V. 42	Unhyd. I.V. 10	Hyd. I.V. 3	Unhyd. I.V. 123	Hyd. I.V. 23	Unhyd. I.V. 86	Hyd. I.V. 52
8:0					6.8	7.0				
10:0					4.8	4.8				
12:0					55.8	56.0				
14:0					17.9	17.9				
16:0	6.8	7.3	10.1	10.9	6.3	6.5	12.5	12.7	12.8	15.2
18:0	1.9	90.5	7.9	40.0	1.6	5.0	1.6	57.0	1.9	5.0
18:1	13.1	0	21.5	47.3	5.3	2.8	24.2	29.7	76.4	74.3
18:2	78.0	1.6	52.6	1.8	1.5	0	60.9	0.2	8.9	5.5
18:3	0.1	0	7.9	0			0.6	0.2		
20:0	0.1	0.6					0.2	0.2		

the irradiation treatment did not significantly alter the fatty acid composition of these fats.

Analysis of volatiles was made on the irradiated samples of the unhydrogenated and the hydrogenated fats as well as their unirradiated controls. In all the fats studied, irradiation resulted in the production of hydrocarbons, aldehydes, methyl esters and ethyl esters (Table II). The hydrocarbon series included the alkanes from C_8 to C_{17}, dienes from C_{10} to C_{17} and some trienes. Examination of the quantitative data shows that the amounts of the various hydrocarbons produced varied significantly with variation in fatty acid composition.

Safflower Oil

Linoleic acid comprised approximately four fifths of the total fatty acids in the unhydrogenated safflower oil (Table I). The two main radiolytic products expected from linoleic acid on the basis of the splitting pattern proposed earlier by Dubravcic and Nawar (5) would be heptadecadiene (the C_n-1 hydrocarbon) and hexadecatriene (the C_n-2 hydrocarbon with an extra double bond). As shown in Table II, these two hydrocarbons were produced in greater quantities than all others and accounted for approximately three fourths of the total hydrocarbons. The other two main hydrocarbons from linoleic acid (i.e., heptadecatriene and hexadecadiene) were also major peaks which accounted for about 8% of the total hydrocarbons. The next highest fatty acid in unhydrogenated safflower oil is oleic acid. The two major radiolytic products, i.e., the $C_{17:1}$ and the $C_{16:2}$ hydrocarbons, were produced in relatively large amounts. Finally, palmitic acid, the third major fatty acid in safflower oil was responsible for the production of the $C_{15:0}$ and the $C_{14:1}$ hydrocarbons, again produced in relatively large amounts. All other hydrocarbons were produced in much smaller quantities and probably resulted from random splitting of the fatty acid chains.

The effect of hydrogenation (i.e., conversion of most of the linoleic and oleic acids into stearic acid) on the radiolytic pattern is quite clear. The $C_{17:2}$, $C_{16:3}$ and $C_{16:2}$ hydrocarbons were practically nonexistent in the hydrogenated fat while the $C_{17:0}$ and the $C_{16:1}$ were remarkably increased (Table II). The relatively significant amount of the C_{17} alkene could also be attributed to stearic acid (5).

The production of aldehydes appears to be also related to the fatty acid composition of the fat. The $C_{16:0}$ acid was present in approximately equal quantities in the unhydrogenated and hydrogenated fats. The $C_{16:0}$ aldehyde, presumably originating from the $C_{16:0}$ acid, was produced in about equal quantities. The high amounts of $C_{18:2}$ and $C_{18:1}$ acids in unhydrogenated oil are reflected in correspondingly high amounts of aliphatic aldehydes with the same number of carbon atoms while the $C_{18:0}$ aldehyde was produced in much larger quantities in the irradiated hydrogenated than the unhydrogenated fat.

No methyl or ethyl esters could be detected in the unhydrogenated oil. However, as shown in Table II, the saturated C_{16} and C_{18} ethyl esters were present in the irradiated, hydrogenated oil in relatively large quantities. When Dubravcic and Nawar (5) irradiated tripalmitin and tristearin, the C_{16} and C_{18} methyl and ethyl esters were produced, but these compounds were absent in irradiated tripalmitolein and triolein. In safflower oil, as well as in the other vegetable fats studied, significantly more of the C_{16} ethyl ester was produced by irradiation in the hydrogenated fat than in the unhydrogenated fat, even when the amount of the C_{16} acid was equal in both fats. This seems to indicate that unsaturation in the medium disfavors the production of ethyl esters.

Unirradiated controls, both unhydrogenated and hydrogenated were practically free of hydrocarbons, aldehydes and methyl or ethyl esters.

Soybean Oil

As in the case of unhydrogenated safflower oil, the presence of a large amount of linoleic acid was reflected in the formation of the $C_{17:2}$ and the $C_{16:3}$ hydrocarbons by irradiation. These two compounds were the radiolytic products produced in the greatest quantities. Similarly, proportional amounts of the $C_{17:1}$ and the $C_{16:2}$ hydrocarbons were produced from oleic acid and so on with the remaining fatty acids. In contrast to safflower oil, however, soybean oil contained approximately 8% of the $C_{18:3}$ acid. This was clearly reflected in the formation of the $C_{17:3}$ and the $C_{16:4}$ hydrocarbons, the two major radiolytic products of linolenic acid (5).

As shown in Table I hydrogenation of soybean oil was only partial and resulted in the elimination of linolenic acid, reduction of linoleic acid to a trace amount and large increases in the amounts of both stearic and oleic acids. These changes correlated well with the composition of hydrocarbons present in irradiated hydrogenated soybean oil, as demonstrated by the following observations in the hydrogenated fat. The formation of the $C_{17:3}$ and the $C_{16:4}$, and the $C_{17:2}$ and the $C_{16:3}$ hydrocarbons was eliminated or markedly reduced, reflecting the elimination of the $C_{18:3}$ and the $C_{18:2}$ acids, respectively. The $C_{17:1}$ and the $C_{16:2}$ were almost doubled reflecting the increase in oleic acid. The $C_{17:0}$ and the $C_{16:1}$ hydrocarbons were formed in larger quantities reflecting the high amount of stearic acid in the hydrogenated fat.

The aldehydes expected on the basis of the composition of the fatty acids in the unhydrogenated and hydrogenated soybean oils were all identified (Table II). The effect of hydrogenation can be

TABLE II
Quantitative Analysis of Products Formed in Unhydrogenated and Hydrogenated Vegetable Oils Irradiated at 6 Megarad and 25 C (μg/100 g fat)

Carbon number	Safflower oil		Soybean oil		Coconut oil		Corn oil		Olive oil	
	Unhyd.	Hyd.	Unhyd.	Hyd.	Unhyd.	Hyd.	Unhyd.	Hyd.	Unhyd.	Hyd.
Hydrocarbons										
8:0	[a]	[a]	0	1290	620	300			[a]	0
8:1	[a]	[a]	Trace	200	710	375	200	[a]	[a]	515
9:0	650	1900	Trace	1290	1150	740	300	[a]	0	970
9:1	Trace[b]	Trace	Trace	Trace	210	20	200	0	0	[a]
10:0	15	18	Trace	[a]	240	[a]	382	640	200	600
10:1	12	50	Trace	[a]	5810	1980	163	80	440	0
10:2	220	0	160	[a]			256	75	15	0
11:0	20	400	37	75	9010	7200	48	175	108	50
11:1	50	80	160	150	806	700	56	67	54	130
11:2	[a]	Trace	[a]	0			56	[a]	[a]	[a]
12:0	25	650	120	150	165	150	Trace	493	150	15
12:1	18	90	80	300	2750	1360	48	94	104	114
12:2	20	Trace	100	0			26	120	Trace	159
13:0	37	870	120	436	3200	3500	12	221	54	40
13:1	15	Trace	80	300	570	392	80	Trace	270	248
13:2	220	100	400	0			Trace	[a]	180	850
14:0	20	850	70	150	57	1294	75	300	120	85
14:1[c]			34	Trace			100	60	250	550
14:1	1395	800	2000	1900	1325	920	2260	2220	2220	1450
14:2	180	[a]	200	Trace	0	0	114	188	270	[a]
15:0	2150	3000	2830	4340	2040	1640	2500	3050	2220	2850
15:1[c]	215	200	150	130	90	546	100	180	176	282
15:1	170	180	150	180	714	134	150	221	232	420
15:2	365	40	150	0	0	0	140	35	196	320
16:0	180	3000	Trace	250	140	[a]	160	464	Trace	120
16:1[c]			810	50			48	30	207	230
16:1	308	10000	Trace	5000	260	620	300	9800	332	350
16:2	3200	0	3500	6500	735	100	3824	4460	13400	8140
16:3	18100	0	16000	0	0	0	6430	0	1200	[a]
16:4			[a]	0						
17:0	Trace	59000	[a]	8400	[a]	1785	[a]	14600	1200	2100
17:1[c]	2000	0			[a]	580	820	3060		
17:1	0	1500	2150	4200	[a]	316	[a]	394	9500	11300
17:2	19300	Trace	20000	600	230	[a]	6420	Trace	3820	3460
17:3	2980	Trace	4100	0	[a]	0	1500	0	320	200
Aldehydes										
10:0					400	Trace				
12:0					[a]	[a]				
12:1					4460	[a]				
14:0					2360	350				
16:0	1400	1500	3560	1240	677	Trace	1600	1500	3700	2820
16:1	140	50	600	100			70	28	274	200
18:0	180	2180	286	610			70	468	170	280
18:1	1160	400	6500	320			2500	94	8250	7360
18:2	11900	0	12000	0			4800	0	9850	7800
18:3			2000	0			2700	0		
Methyl esters										
10:0					Trace	1000				
12:0					[a]	[a,d]				
14:0					Trace	[a,d]				
16:0	0	[a]	[a]	100	Trace	[a,d]	[a]	1420		
18:0	0	[a]	[a]	75			0	[a]		
Ethyl esters										
8:0					0	1100				
10:0					Trace	585				
12:0					Trace	[a,d]				
14:0					Trace	[a,d]				
16:0	0	1800	Trace	1670	0	[a,d]	0	1420		
18:0	0	[a]	0	800			0	1430		

[a] Present but could not be quantitatively determined due to overlap.
[b] Trace, less than 10 μg/100 g fat.
[c] Unsaturation is internal and not terminal.
[d] Large amount indicated by mass spectra.

observed by the absence of the $C_{18:2}$ and the $C_{18:3}$ aldehydes. However, the amounts of aldehydes formed were not always closely proportional to the fatty acids as was the case in hydrocarbon production.

As in the case of safflower oils, there was little, if any methyl or ethyl esters in the unhydrogenated oil. Ethyl esters, however, were present in relatively large quantities in the case of hydrogenated fat.

Coconut Oil

Of all the samples studied, coconut oil exhibits the largest variety of fatty acids; it contains the saturated acids from caproic to stearic acids in addition to oleic and linoleic acids. The unsaturated acids comprised only about 7% of the total fatty acids and hence the effect of hydrogenation was limited to this small fraction (Table I). The presence of short chain saturated acids in both the unhydrogenated and hydrogenated coconut oils resulted in the formation by irradiation of the typical corresponding major hydrocarbons expected on the basis of the breakdown pattern discussed earlier (Table II). Thus the two hydrocarbons formed in the greatest quantity were the $C_{11:0}$ and the $C_{10:1}$ obviously originating from the $C_{12:0}$ acid which comprises more than half of the total fatty acids content of coconut oil. Similarly, the two major compounds resulting from each of the $C_{10:0}$, $C_{14:0}$, $C_{16:0}$ and $C_{18:0}$ acids can be clearly accounted for.

While aliphatic aldehydes typical of those resulting from irradiation of short chain fatty acids were detected in both the unhydrogenated and the hydrogenated samples, the quantitation of such aldehydes was difficult due to their overlap with the longer chain hydrocarbons. The mass spectra of these aldehydes gave indication of the presence of more than one compound. Traces of methyl and ethyl esters were found in the unhydrogenated irradiated oil but these compounds were present to a much greater extent in hydrogenated irradiated sample. Only traces of the $C_{10:0}$, $C_{12:0}$, $C_{14:0}$ and $C_{16:0}$ methyl and ethyl esters were detectable in the control samples.

Corn Oil

The pattern of hydrogenation was somewhat similar in the case of corn oil to that of soybean oil except that hydrogenation proceeded to a higher

degree, as reflected both in fatty acid composition and iodine values (Table I). The disappearance of linoleic acid and the appearance of stearic acid in hydrogenated oil was more pronounced. Oleic acid increased in amount in the hydrogenated sample. These changes clearly determined the relative proportions of the various hydrocarbons present in their volatiles. Thus the two largest peaks in unhydrogenated oil, namely the $C_{17:2}$ and $C_{16:3}$ hydrocarbons (radiolysis products of linoleic acid), were virtually replaced by $C_{17:0}$ and $C_{16:1}$ (radiolysis products of stearic acid). The proportions of other major hydrocarbons can be similarly explained on the basis of the fatty acids present in the fat.

The aldehydes present were in fair agreement with the fatty acid composition of the oils. However, in the case of the hydrogenated sample, the $C_{18:1}$ aldehyde was present in a much smaller amount. It is difficult to explain this anomaly at present.

Olive Oil

The major fatty acid in olive oil is oleic acid. As expected, the $C_{17:1}$ and $C_{16:2}$ hydrocarbons were produced in relatively large quantities by irradiation. Since hydrogenation of olive oil was allowed to proceed only to a small degree, the radiolytic products of the unhydrogenated and the hydrogenated samples were not too different. However, the amount of heptadecane, the major radiolytic product of stearic acid, was approximately twice as much in the hydrogenated fat as in the unhydrogenated sample.

The methyl and ethyl esters of palmitic and stearic acids were detected in the unirradiated control samples in fairly large quantities. For this reason and because of considerable overlap in the gas chromatograms, it was difficult to ascertain the effect of irradiation on the formation of methyl and ethyl esters in olive oil. No hydrocarbons or aldehydes were present in the unirradiated samples.

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