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Comparison of oxidation of sucrose octaesters and triacylglycerols derived from olive oil

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Pure Sucrose Octaesters (SOE) and Triacylglycerols (TG) with the same fatty acid composition were oxidized at 100°C for 3, 6 and 12 h, in triplicate. Quantification of oxidized substrates and oxidized fatty acids was carried out by a combination of adsorption and size exclusion chromatographies. Induction time periods, peroxide values and changes in fatty acids were also determined. The results indicated that triacylglycerols were oxidized more rapidly than sucrose octaesters. No prooxidant effect of triacylglycerols on the oxidation of sucrose octaesters was found when a mixture (1:1) of both of them was subjected to oxidation.

INTRODUCTION

Extensive research has been carried out to find the perfect fat substitute having the functional and sensory properties of fats but with as few calories as possible (Gillis, 1988; LaBarge, 1988). Among the possible substitutes, sucrose polyester (SPE) stands out. It has been the subject of numerous investigations recently reviewed from different points of view (Jandacek, 1984; Boggs, 1986; Toma *et al.*, 1988; Harrigan & Breene, 1989), and is pending approval by the Food and Drug Administration (FDA). SPE is a non-caloric fat containing 5–8 fatty acids esterified to a sucrose molecule. Those fatty acids determine the physical properties of the resulting fat, ranging from solid to liquid state. Sucrose polyester is resistant to lipase action, hence its non-absorption and its non-caloric nature.

In contrast to other fat substitutes, which can only be used at low temperature due to their chemical nature, SPE can also be used in baking and frying. If approved by the FDA, SPE could comprise up to 35% of fats in home cooking oils and shortenings, and 75% of those in commercial cooking oils and snack foods (Anon, 1990).

Given the possibility of its use at high temperature, it is important to know the susceptibility of SPE to thermal, oxidative, and hydrolytic modifications undergone by fats during food preparation processes.

A few papers have been published comparing the oxidative rate of free fatty acids and their esters (Holman, 1954; Miyashita & Takagi, 1986; Takagi & Miyashita, 1987), but no references on the sucrose esters have been found.

The aim of this work was to study the behaviour under oxidative conditions of SOE compared to TG with similar fatty acid compositions, with special reference to the determination of the main groups of polar compounds (monomers and dimers) originating during oxidation.

MATERIALS AND METHODS

Synthesis and purification of sucrose octaesters and triacylglycerols

Sucrose polyesters were prepared according to the solvent-free, sucrate-catalysed method of Rizzi & Taylor (1978), starting from sucrose and fatty acid methyl esters derived from olive oil. The final yield was 39% of theoretical. Analysis by thin-layer chromatography (Rizzi & Taylor, 1978) indicated the presence of sucrose esters containing 5–8 fatty acyl moieties per sucrose molecule. Triacylglycerols were obtained by esterification of fatty acids from the same olive oil and glycerol, using *p*-toluene sulphonic acid as catalyst

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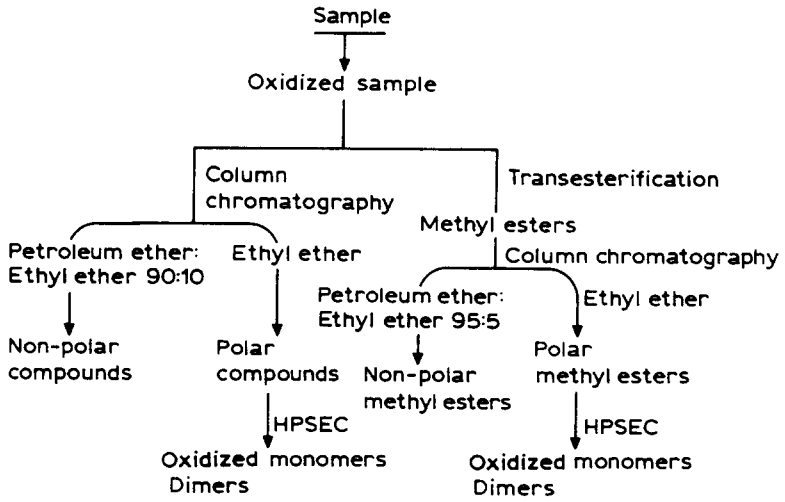

Fig. 1. Scheme for the analysis of oxidized samples.

(Hilditch & Rigg, 1935). The final yield was 78% of theoretical.

Isolation and purification of sucrose octaesters (SOE) and triacylglycerols (TG) were carried out by means of silica column chromatography as follows.

50 g of SPE or TG dissolved in petroleum ether:ethyl ether (96:4) was transferred to a column (4·5 cm i.d. × 42 cm) containing 320 g of silica gel suspended in the same mixture of solvents. A first fraction eluted with 1·5 litres of petroleum ether:ethyl ether (96:4), contained minor non-polar impurities and was discarded. A second fraction eluted with 1·5 litres of petroleum ether:ethyl ether (90:10) contained pure SOE or TG without contamination by the more polar compounds. This was the fraction used in this study. 28 g of pure SOE and 42 g of pure TG were recovered.

Infrared spectra of the purified compounds were recorded as thin films using a Perkin-Elmer 782 Infrared Spectrophotometer. The spectra indicated the absence of free hydroxyl groups in both samples. Purity was greater than 99% by thin-layer chromatography (Rizzi & Taylor, 1978) and exclusion chromatography (Birch & Crowe, 1976).

Sample treatment

Samples of 2 g of SOE, TG and a mixture 1:1 (wt %) of both of them were oxidized in triplicate under controlled conditions (100°C and 15 litres/h air). After oxidization for 3, 6 and 12 h, samples were stored at –25 °C until analysis.

Analytical determinations

1. Induction time period was determined by the Rancimat Method at 100°C (Läubli & Bruttel, 1986).
2. Peroxide value (PV) was estimated by AOCS Standard Method (1990).
3. Fatty acid composition was performed by gas–liquid chromatography (GLC) following transesterification of the sample with CH_3ONa and HCl– CH_3OH. A column 2 m long, 1/8 in i.d. packed with 15% DEGS on Supelcoport, 80–100 mesh, and at a temperature of 180°C was used.
4. Percentage and distribution of polar compounds and polar fatty acids were determined by a combination of adsorption and size exclusion chromatographies (Dobarganes *et al.*, 1988; Márquez-Ruiz *et al.*, 1990). The analytical procedure is summarized in Fig. 1.

RESULTS AND DISCUSSION

Table 1 shows the induction time periods for the three samples, and the change of peroxide values with oxida-

Table 1. Induction time periods and evaluation of peroxide values during oxidation at 100 °C

Sample	Induction time period (h)		Peroxide value (meq/kg)						
			0 h	3 h		6 h		12 h	
	X[a]	S_x[b]		X	S_x	X	S_x	X	S_x
SOE	4·6	0·40	0	72	7·8	198	14·9	546	15·0
TG	2·2	0·20	0	235	13·7	385	38·8	1046	75·3
SOE:TG (1:1)	3·1	0·26	0	116	16·4	429	29·9	802	47·3

[a] Means of three determinations.
[b] Standard deviation.

Table 2. Fatty acid distribution and induction time period in the initial olive oil and after randomization

		Fatty acid distribution (%)					Induction time period (h)
		$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	Others	
Initial olive oil	Total fatty acids	11·2	2·8	75·7	9·1	1·2	12·3
	2-position	0·9	0·2	85·3	11·7	1·9	
TG after randomization	Total fatty acids	10·9	2·9	75·5	9·2	1·5	2·2
	2-position	11·1	3·0	75·0	9·5	1·4	

tion time. The values obtained indicate a significantly greater stability of SOE, which had an induction time period more than twice that of TG. The peroxide values for SOE are very much lower for the same treatment period.

Triacylglycerols were synthesized to eliminate differences due to specific fatty acid distribution in natural vegetable oils. Table 2 shows fatty acid distribution in the original olive oil and after transesterification and purification of randomized TG. Fatty acids in the 2-position were determined after enzymatic hydrolysis with pancreatic lipase (IUPAC, 1987). Induction time periods for both samples have been included in the last column of the table. As can be observed, after randomization no differences have been found between total fatty acids and fatty acids in the 2-position, confirming randomization. Surprisingly, the induction time period for randomized TG was much lower than for the initial olive oil, which may be attributed to a loss of antioxidants.

The sample triplicates obtained after each oxidation period were used as a single sample prior to analysis of fatty acids and polar compounds.

The similar fatty acid compositions of the initial samples are shown in Table 3, which also shows the modification undergone by the major fatty acids after 3, 6 and 12 h of oxidative treatment. As can be seen, there is a marked decrease in linoleic acid and an apparent increase of saturated acids. Assuming that the latter do not suffer significant alteration under these conditions, an approximate calculation of the amounts of unaltered fatty acid can be obtained maintaining the saturated fatty acids quantities at initial levels (Dobarganes & Pérez-Camino, 1988; Yoon *et al.*, 1987). The results obtained are included in the last column of the table, and confirm that oxidation of the fatty acids was more rapid when esterified in the glycerol molecule. In all cases, the values obtained for the mixture are intermediate between those for pure SOE and TG.

Table 4 summarizes the results obtained after quantification of polar compounds and polar acids by means of adsorption chromatography on a silica column, following the procedure shown in Fig. 1.

The efficiency of the separation has been confirmed using TLC and is shown in Fig. 2 for the samples of SOE and TG after 6 h of oxidation. As can be seen, the polar compounds include all the compounds originating during the oxidative treatment. The non-polar fraction is qualitively identical to the initial sample, and contains the non-altered compounds.

The values obtained in the evaluation of the polar compounds are in principle surprising, as they indicate that, after 12 h of treatment, the oxidized quantities

Table 3. Changes in fatty acid composition after oxidation for 3, 6 and 12 h (%)

		$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	Others	Non-altered fatty acid[a]
0 h	SOE	10·9	2·7	75·8	9·5	1·1	100
	TG	10·9	2·9	75·5	9·2	1·5	100
	SOE:TG (1:1)	11·3	2·8	75·0	9·4	1·5	100
3 h	SOE	11·2	2·8	75·6	8·8	1·6	97·1
	TG	12·0	3·1	76·0	7·4	1·5	91·4
	SOE:TG (1:1)	11·9	3·3	75·2	8·0	1·6	92·8
6 h	SOE	12·2	3·4	76·2	6·8	1·4	87·2
	TG	14·0	3·8	77·2	3·8	1·2	77·5
	SOE:TG (1:1)	13·6	3·4	76·0	6·0	1·0	83·9
12 h	SOE	13·7	3·8	77·2	4·3	1·0	77·7
	TG	16·6	4·2	77·4	1·0	0·8	66·3
	SOE:TG (1:1)	15·6	4·0	76·9	2·8	0·7	71·9

[a] Values calculated assuming no alteration in initial saturated fatty acids ($C_{16:0}$ + $C_{18:0}$).

Table 4. Quantitation of total polar compounds and total polar fatty acid methyl esters after oxidation for 3, 6 and 12 h (wt% on fat)

	Sample	3 h	6 h	12 h
Polar compounds from:	SOE	22·7	60·4	79·6
	TG	33·9	65·2	71·8
	SOE:TG (1:1)	33·2	65·0	75·7
Polar methyl esters from:	SOE	4·1	13·5	21·3
	TG	11·1	27·6	35·2
	SOE:TG (1:1)	9·0	21·9	30·5

of SOE are greater than those of TG. These values may seem contrary to those obtained for the evolution of peroxides and fatty acids. Nevertheless, the results are easily explained by taking into account the different molecular structures of SOE and TG, which have 8 and 3 acyl groups respectively. Since oxidation takes place in the unsaturated fatty acyls of the molecule, it is readily deduced from their different structures that the same quantity of oxidized SOE or TG may give rise to up to almost three times more polar fatty acids in the case of TG.

The quantitation of oxidized or polar acids after transesterification, included in the lower part of Table 4, proves this simple fact beyond doubt. As can be seen, the quantities of oxidized acids are markedly lower in the case of SOE, as expected from its greater induction time period. The ratio (% polar acids/ % polar compounds)100 which indicates the percentage of oxidized acids in the molecule, ranges between 33 and 49 for the triglycerides, between 18 and 27 for SOE, and between 27 and 40 for the mixture of both.

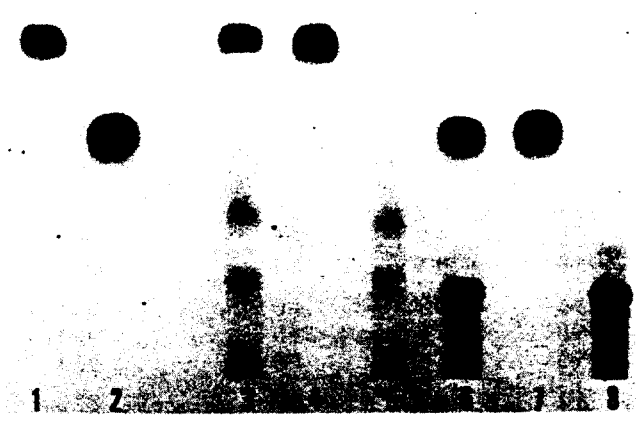

Fig. 2. Thin layer chromatography (petroleum ether:ethyl ether:acetic acid — 65:35:1) showing original samples and separations of oxidized samples following the scheme in Fig. 1. 1, sucrose octaesters; 2, triacylglycerols; 3, oxidized sucrose octaesters; 4, 5, non-polar and polar fractions from 3; 6, oxidized triacylglycerols; 7, 8, Non-polar and polar fractions from 6.

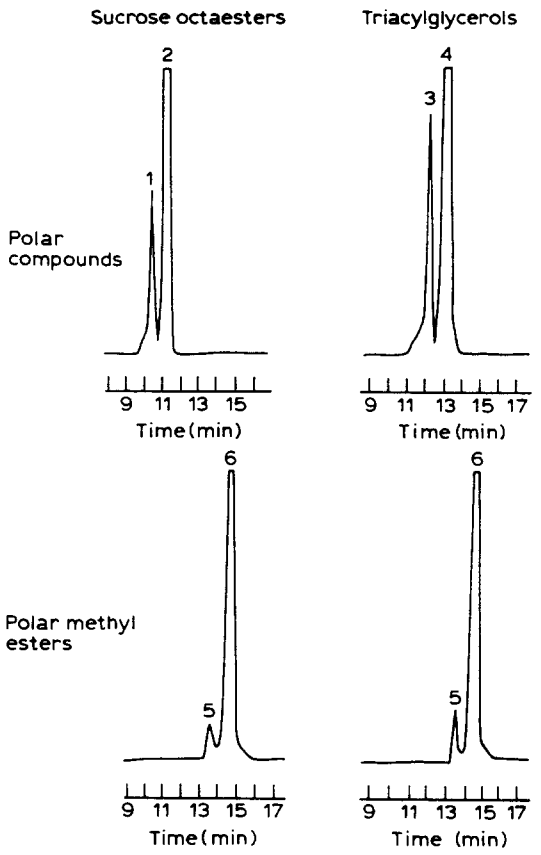

Fig. 3. Chromatograms of polar compounds after 6 h of oxidation (upper part), and polar fatty acid methyl esters (lower part) (for peak identification see Table 5).

This clearly demonstrates the greater concentration of oxidized acids in the TG molecule. Finally, no synergistic effect of TG on the oxidation of SOE has been observed, as similar values are found for the oxidation of the SOE:TG mixture and the theoretical ones that can be expected.

Separation of the oxidation compounds by means of high performance size exclusion chromatography (HPSEC) has allowed the quantitative determination of the main groups of compounds formed. Chromatograms of the polar compounds of the samples after 6 h of oxidation are shown in the upper part of Fig. 3, and, in its lower part, those for the fraction of oxidized or polar acids of the same samples. The principal groups of new compounds originated as a consequence of the oxidative treatment and their corresponding retention times are summarized in Table 5. It must be pointed out that separation and quantification by HPSEC was only possible through prior elimination of the unaltered fraction of the samples, as the compounds included in the non-polar fraction have identical retention times (Rt) to the oxidized monomers.

Table 6 summarizes the quantitative results obtained. Quantitation of the mixture SOE:TG (1:1) has not been included in the table as the retention times for the TG

Table 5. Main groups of polar compounds present in oxidized samples: retention times and peak numbers after separation by HPSEC

	Abbreviation	Retention Time (min)[a]	Peak Number
Dimeric sucrose octaesters	D SOE	10·8	1
Oxidized monomer sucrose octaesters	OM SOE	11·7	2
Dimeric triacylglycerols	D TG	11·9	3
Oxidized monomer triacylglycerols	OM TG	12·7	4
Dimeric fatty acid methyl esters[b]	D FA	13·6	5
Oxidized monomer fatty acid methyl esters[b]	OM FA	14·6	6

[a] ± 0·1 min.
[b] Obtained after transesterification of oxidized samples.

dimers and oxidized monomers of SOE are very similar and a single peak is obtained. Moreover, dimeric compounds combining SOE and TG molecules can be expected. Recently characterization of high molecular weight compounds in thermally oxidized SPE has been reported (Gardner & Sanders, 1990)

Basically, monomeric and, in lower amounts, dimeric compounds are obtained at the temperature used. After 12 h of oxidation, the presence of compounds with higher molecular weight is already perceptible. However, no appreciable quantities of compounds with molecular weights lower than those of the initial compounds were observed in any of the samples.

In conclusion, the results obtained in this study indicate that the oxidation of SOE takes place more slowly than that of the TG with a similar fatty acid composition when starting from pure compounds. Given the importance of the small amounts of antioxidant or prooxidant compounds and of the natural fatty acids distribution in the stability of fats, it is not possible to extrapolate the results to the comparison of natural fats with SPE. As previously mentioned, the original olive oil induction time period was much higher than that of both TG and SOE.

At present, similar experiments are being carried out to determine the susceptibility of SPE to hydrolysis and its behaviour at high temperature ≈ 200°C under conditions of restricted oxidation.

Table 6. Distribution of polar compounds and polar fatty acid methyl esters after oxidation for 3, 6 and 12 h (wt% on fat)

	Sample	Oxidized compound	3 h	6 h	12 h
Polar compounds from:	SOE	OM SOE	18·8	47·5	59·2
		D SOE	3·9	12·9	20·4
	TG	OM TG	24·6	49·2	52·6
		D TG	9·2	16·0	19·2
Polar methyl esters from:	SOE	OM FA	3·5	11·9	18·3
		D FA	0·6	1·6	3·0
	TG	OM FA	8·3	22·7	28·1
		D FA	2·8	4·9	7·1
	SOE:TG (1:1)	OM FA	7·7	18·6	25·7
		D FA	1·3	3·3	4·8

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