Changes in molecular species of triacylglycerols during frying

By **Gary Dobson** (1), **William W. Christie** (1) **and M.C. Dobarganes** (2)

(1) Scottish Crop Research Institute, Invergowrie, Dundee (DD2 5 DA), Scotland
(2) Instituto de la Grasa (C.S.I.C.), 41012 Sevilla, Spain

SUMMARY

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The loss of specific molecular species of triacylglycerols from sunflower, high-oleate sunflower and palm oils has been investigated in commercial frying operations and simulated frying experiments. The non-oxidized triacylglycerols were isolated and molecular species separated by silver ion high-performance liquid chromatography. Linoleate-containing species were lost more rapidly than those containing oleate, as expected. However, all species were liable to oxidation and those containing oleate were lost more rapidly than might have been anticipated. It is suggested that oxidation of linoleate is the probable initiation step, but then the reaction can be propagated readily to all unsaturated species.

KEY-WORDS: Frying – High oleic sunflower oil – Molecular species of triacylglycerols (loss) – Palm oil – Sunflower oil

1. INTRODUCTION

The chemistry and reactivity of natural fats and oils is dependent mainly on their overall composition and especially on the relative composition of the fatty acid constituents. In addition to this, the structures of the fats in terms of the relative proportions of different molecular species or of the stereospecific distributions of fatty acids on the glycerol moieties have a bearing on their properties. One of the primary concerns in using unsaturated oils for frying purposes is that increased oxidation will be a problem. During frying, oils are subjected to prolonged heating at a temperature around 180°C, and are subject to attack by atmospheric oxygen in the presence of water and food components. Autoxidation can occur catalysed by traces of heavy metals that may be present. The topic has been reviewed elsewhere (Blumenthal, 1987; St Angelo, 1992).

It might be expected that more highly unsaturated molecular species of triacylglycerols would be lost preferentially. We investigated the changes that occurred in the molecular species of triacylglycerols in sunflower oil, high-oleate sunflower oil and palm oil during commercial frying and in simulated frying experiments. In the former, the oil was replenished continuously to maintain a constant level of oil as fried products (potato crisps) were removed. The experimental approach was to examine the residual non-oxidised fraction of the oil by analysing molecular species by silver ion high-performance liquid chromatography (HPLC).

2. MATERIALS AND METHODS

2.1. Sample preparation

Triacylglycerols were purified from the oils supplied from the frying trials by column chromatography on solid-phase extraction columns of silicic acid (Isolute™ 500 mg; International Sorbent Technology; Hengoed, Wales). The oil (0.5 mL) was applied to the column in isohexane-acetone (99:1, v/v) and pure triacylglycerols were eluted with 30 mL of this solvent. Purity was confirmed by TLC (Merck Silica gel 60; 0.2 mm layers) with isohexane-diethyl ether-acetic acid (80:20:1 by volume) as developing solvent with iodine to visualise the spots.

2.2. Silver ion high-performance liquid chromatography

Triacylglycerols (0.5 mg in dichloromethane) were fractionated by silver ion HPLC using a column of Nucleosil™ 5SA (250 x 4.6 mm i.d.), converted to the silver ion form, as described elsewhere (Christie, 1987). The elution conditions were also published earlier (Christie, 1988). In brief, the column was eluted with a gradient of dichloromethane-dichloroethane (1:1, v/v) (Solvent A), acetone (Solvent B) acetone-acetonitrile (9:1, v/v) (Solvent C). There was a linear gradient of 100% A to 50% A - 50% B over 15 minutes, then to 50% B - 50 % C over a further 40 min at a flow-rate of 1 mL/min. A Cunow DDL-21 evaporative light-scattering detector (Cergy St. Christophe, France) was used with a stream splitter between the detector and the column.

2.3. Gas chromatography

A standard solution of methyl heptadecanoate was added to each fraction as an internal standard for subsequent quantification by gas chromatography (GC), following trans-methylation with sodium methoxide (Christie, 1982).

Methyl esters of fatty acids were analysed on a Carlo Erba Model 4130 capillary gas chromatograph (Erba Science, Swindon, U.K.), fitted with split/splitless injection, and equipped with a capillary column (0.25 mm i.d. x 25 m in length) of fused silica coated with Carbowax 20M (Chrompack UK Ltd, London). After holding the temperature at 175°C for 3 min, it was temperature-programmed at 3°C/min to 205°C, then was held at this point for a further 10 minutes. Hydrogen was the carrier gas. Components were quantified by electronic integration.

2.4. Frying procedures

Three commercial electric fryers, containing 1 L of either, sunflower oil, high-oleate sunflower oil or palm oil, were used to prepare three lots of 3 Kg of French fries. Potatoes were peeled, cut into homogeneous strips, and washed with water. Thirty batches, each of 100 g of potato strips, were fried for 6 min, and intervals of 6 min were established between frying operations. Thus oils were heated over a total period of 6 hours. The temperature was monitored during the experiment, and it never rose above 200°C and it did not drop below 140°C when fresh potato strips were immersed in the oil. No replenishments of the oil were made during frying, and the surface to volume ratio changed from 0.32 to 0.64.

Oils with various degrees of oxidation, up to 56%, were also obtained from similar experiments in which the oils were heated in the absence of potato strips.

2.5. Determination of degree of oxidation

The degree of oxidation of the samples was determined by silica column chromatography, following the standard method proposed by IUPAC (1987) with a minor modification, *i.e.* petroleum ether-ethyl ether 90:10 v/v (instead of 87/13) was used to elute the nonpolar fraction.

3. RESULTS AND DISCUSSION

The nature of the commercial frying experiments are described elsewhere. Samples of each oil were taken during and at the end of the commercial frying trials involving crisp production, and the unchanged triacylglycerols (oxidised materials removed) were isolated. The fatty acid composition of each oil was determined by GC of the methyl ester derivatives, and the molecular species composition by silver ion HPLC (followed by transesterification and GC analysis). As an example, Figure 1 illustrates the separation of molecular species of triacylglycerols from high-oleate sunflower oil. The trace trisaturated component is eluted first, followed by fractions with an increasing degree of unsaturation. The fatty acid compositions of the oils and of the various molecular species of each are listed in Table I. As expected sunflower oil contains high proportions of linoleate-rich species, high-oleate sunflower oil contains more than 50% triolein, and palm oil has greater amounts of more saturated species. In each analysis as a check on the quality of the data, the fatty acid composition of the total oil was computed from the compositions of the fractions the total, and good agreement was always obtained.
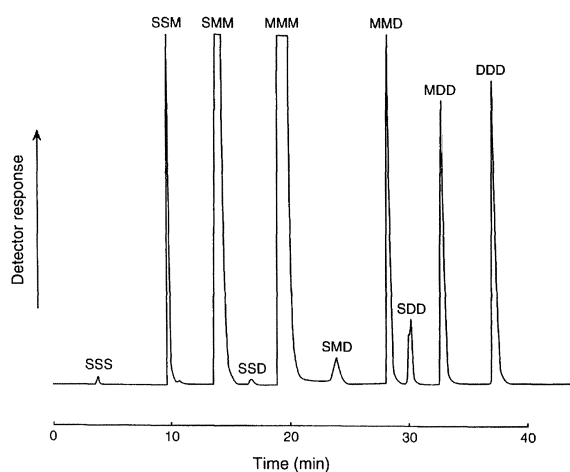

Figure 1
Silver ion HPLC separation of molecular species of triacylglycerols from high-oleate sunflower oil. See text for experimental conditions.
Abbreviations: S = saturated, M = monoenoic, D = dienoic fatty acids, respectively

Table I
Triacylglycerol fractions from silver ion HPLC of the oils used in the frying trials

Fatty acid	Total	Check	SSS[a]	SSM	SMM	SSD	MMM	SMD	MMD	SDD	MDD	DDD
Sunflower Oil												
16:0	7.3	6.9		38.6	15.9	38.1	1.3	18.8	0.4	17.4	–	–
18:0	4.5	4.7		24.9	11.5	25.0	1.0	11.2	0.3	12.5	–	–
18:1(n–9)	20.6	20.3		36.6	71.7	1.1	93.2	34.1	62.4	0.4	31.0	–
18:1(n–7)	0.5	0.5		–	0.9	–	1.4	0.8	1.6	–	0.8	–
18:2	67.1	67.6		–	–	35.8	3.1	35.1	35.3	69.7	68.1	100.0
% Fraction				0.7	2.0	3.6	1.9	9.3	8.5	18.4	26.6	29.0
High Oleate Sunflower Oil												
16:0	4.8	4.6		33.3	14.3	33.8	–	17.0	–	17.1	–	–
18:0	4.0	4.2		26.9	14.7	22.3	–	12.4	–	13.5	–	–
18:1(n–9)	74.2	74.1		39.7	71.0	15.0	99.4	35.7	65.8	2.1	32.1	1.6
18:1(n–7)	0.4	0.4		–	–	–	0.6	0.6	0.5	–	0.6	–
18:2	16.6	16.7		–	–	28.8	–	34.2	33.7	67.3	67.4	98.4
% Fraction				1.6	17.5	0.8	52.5	3.8	7.6	3.7	7.0	5.5
Palm Oil												
14:0	1.2	0.7	14.0	1.8	0.2	0.5	–	0.3	–	–	–	–
16:0	37.5	35.7	59.2	57.5	27.1	55.1	0.6	28.2	3.4	25.7	10.0	–
18:0	3.8	3.9	26.8	5.8	3.2	5.2	–	2.7	0.6	3.4	1.9	–
18:1(n–9)	46.0	47.3	–	34.9	68.6	4.6	97.9	34.2	60.8	2.0	33.7	–
18:1(n–7)	0.6	0.6	–	–	0.9	–	1.6	0.4	1.6	–	1.1	–
18:2	11.0	11.7	–	–	–	34.6	–	34.2	33.5	68.9	53.3	100.0
% Fraction			0.2	0.7	26.2	35.0	10.8	6.7	13.7	3.4	2.5	0.9

[a] S = saturated, M = monoenoic, D = dienoic fatty acids, respectively

There were no discernible differences in the fatty acid compositions or the relative proportions of any of the molecular species, even the highly unsaturated ones such as trilinolein, during or at the end of the frying experiment. In these frying trials, the oil was replenished as it was used up and the amount of oxidised material in the oil remained relatively low (<10%).

In batch frying, oil may be used continuously without replenishment, as occurs in many smaller commercial operations; the amount of oxidized oil increases substantially and the amount of unoxidized triacylglycerols is reduced proportionately. Therefore, laboratory-scale frying experiments were conducted to determine the changes that occur as an oil is used for frying over a long period. The results of one experiment with sunflower oil, high-oleate sunflower oil and palm oil are listed in Table II, in which chips (French fries) were prepared, and oil was heated at a temperature that did not exceed 200°C for up to 6 hours. The oils contained 23 to 29% oxidized material at this time, i.e. very similar amounts despite the substantial differences in fatty acid composition. Again, the oil was separated into polar (oxidized) components and non-polar (unoxidized) triacylglycerols by absorption chromatography, before the latter were separated into molecular species by silver ion high-performance liquid chromatography. The proportions of each molecular species lost during oxidation was then calculated by difference. This indirect approach was necessary as it is not possible to analyse molecular species of oxidized triacylglycerols directly.

With all the oils, the more highly unsaturated species are oxidized preferentially as might be expected. Thus, in the linoleate-rich sunflower oil, the greatest loss was of trilinolein and then of the dilinoleoyl species. There were also marked losses of these fractions in palm oil, but together with substantial losses of dioleoyl species. In high-oleate sunflower oil, there was an appreciable loss of triolein, which is a major component in this instance. Species containing a high proportion of linoleate were lost at roughly 2-3 times the rate for oleate.

It appears that most unsaturated species can serve as substrates for oxidation when they are abundant in the oil. However, it has been reported that

linoleate is twenty times as susceptible as oleate to autoxidation (Holman, 1971). Presumably, this result was obtained in experiments with pure compounds. It is very evident from our data that this does not occur in natural oils under conditions of practical interest. It seems in any natural oil that contains significant amounts of linoleate, this may be the primary reactant initiating oxidation. However, subsequent propagation of the reaction with formation of oxidised products may occur only a little less rapidly with molecular species of triacylglycerols containing oleate than with those containing linoleate.

This conclusion was also obtained from experiments in which heated oils containing oxidised material at levels up to 56% were studied. The results for the major molecular species, i.e. trilinolein from sunflower oil and of triolein from high-oleate sunflower oil, are illustrated in Figure 2. The amount of loss of each is linearly related to the degree of oxidation, although the trilinolein species is lost more rapidly as expected.
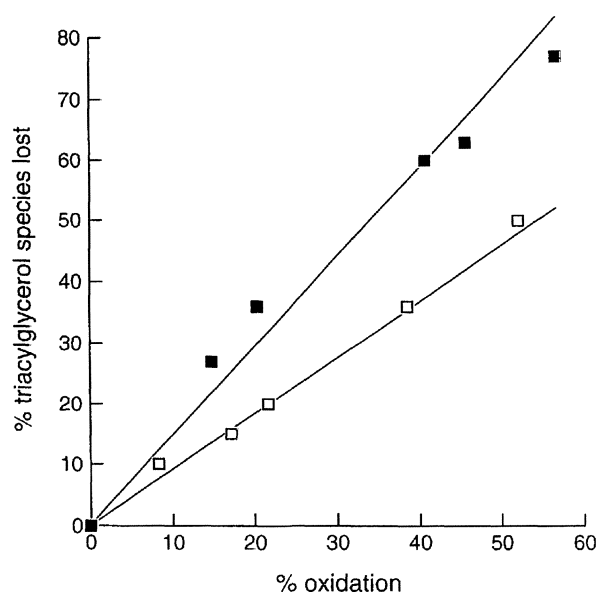

Figure 2
Losses of trilinolein from sunflower oil (■) and of triolein (□) from high-oleate sunflower oil in relation to the amount of oxidised material (degree of oxidation) of the oil

Table II
Oxidation of triacylglycerol molecular species in laboratory-scale frying experiments

	Proportions (%) of molecular species remaining in unoxidised oil after 6 hours[a]			Relative proportion (%) of molecular species lost after 6 hours		
	SO[b]	HOSO	PO	SO	HOSO	PO
SSS	–	–	1.1	–	–	–
SSM	1.2	2.3	30.5	–	–	13
SMM	3.6	20.9	36.4	–	8	23
SSD	3.8	1.3	8.9	25	–	39
MMM	4.2	53.4	7.5	–	22	16
SMD	11.1	3.5	10.6	15	29	42
MMD	9.5	7.3	2.3	20	26	50
SDD	19.9	3.0	1.7	23	38 }	
MDD	24.8	5.3	0.7	34	41 }	47
DDD	21.9	3.2	0.2	46	55 }	
% Oxidized material				28.9	23.0	25.5

[a] Data obtained at intermediate points are not listed.

[b] SO = sunflower oil, HOSO = high-oleate sunflower oil, PO = palm oil

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