The influence of natural tocopherols during thermal oxidation of refined and partially hydrogenated soybean oils

By **C. J. Steel[1], M. C. Dobarganes[2] and D. Barrera-Arellano[1*]**

[1] Laboratório de Óleos e Gorduras, Departamento de Tecnologia de Alimentos, Faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas (UNICAMP) - CEP 13083-970 - Campinas, SP, BRAZIL. daniel@fea.unicamp.br
[2] Instituto de la Grasa (CSIC), Avda. Padre García Tejero, 4 - 41012 - Sevilla, SPAIN

RESUMEN

Influencia de los tocoferoles naturales durante la ter-moxidación de aceites de soja refinados y parcialmente hidrogenados .

Muestras de aceites refinados y parcialmente hidrogenados de soja, con índices de yodo entre 60 y 130, tratadas o no con óxido de aluminio para eliminar los tocoferoles naturales presentes en los aceites, fueron sometidas a termoxidación, a 180°C durante 10 horas. Se tomaron muestras en los tiempos 0, 2, 5, 8 y 10 horas, para determinación de dímeros y polímeros (compuestos de degradación) y de tocoferoles. Se verificó la relación del índice de yodo con la formación de dímeros y polímeros, y también el papel de los tocoferoles originales del aceite y de las grasas en la protección contra la degradación térmica. Las curvas de degradación de los tocoferoles mostraron la destrucción más rápida de α y γ-tocoferoles, respecto a β y δ-tocoferoles. Además, la degradación de los tocoferoles ocurrió a mayor velocidad en las grasas más saturadas. La formación de dímeros y polímeros fue mayor en el aceite que en las muestras hidrogenadas y en las muestras tratadas con óxido de aluminio respecto a sus originales sin tratar.

PALABRAS-CLAVE: Aceites - Degradación térmica - Grasas hidrogenadas - Soja - Termoxidación - Tocoferoles.

SUMMARY

The influence of natural tocopherols during thermal oxidation of refined and partially hydrogenated soybean oils.

Samples of refined and partially hydrogenated soybean oils, with iodine values between 60 and 130, tocopherol-stripped or not by aluminium oxide treatment, were submitted to thermal oxidation, at 180°C for 10 hours. Samples were collected at 0, 2, 5, 8 and 10 hours, for the determination of dimers and polymers (degradation compounds) and tocopherols. The relation of iodine value to the formation of dimers and polymers and the role of originally present tocopherols in the protection of fats and oils against thermal degradation was verified. The degradation curves for tocopherols showed that α and γ-tocopherols were destroyed faster than β and δ-tocopherols. In addition, the degradation rate of tocopherols was greater in the more saturated fats. The formation of dimers and polymers was greater in the oil than in the hydrogenated samples and in the samples treated with aluminium oxide with respect to the original, untreated samples.

KEY-WORDS: Hydrogenated fats - Oils - Soybean - Thermal degradation - Thermal oxidation - Tocophero

1. INTRODUCTION

The quality of fats and oils used for frying is of great importance to the quality of the final product, as the frying oil absorbed by the food product will be consumed as part of it. Values of 5 to 40% absorption of frying oil have been reported for different types of fried foods (Rossell, 1998).

During the frying process, at the same time that desired organoleptic characteristics of color, flavor and odor are developed in the food product, the fat or oil undergoes a complex degradation process, mainly due to the action of three variables – moisture, temperature and oxygen – which produce the most drastic changes in its structure (Pérez-Camino et al., 1988). The fats or oils decompose forming volatile and non-volatile products that alter their functional, organoleptic and nutritional properties (Warner, 1997).

The main degradation products absorbed by the food are the non-volatile, which include triacylglycerol polymers, triacylglycerol dimers, oxidized triacylglycerol monomers, cyclic substances and hydrolytic decomposition products (diacylglycerols, monoacylglycerols and free fatty acids) (Warner, 1997). Broadly, the non-volatile decomposition products can be grouped as the polar fraction, the non-polar fraction corresponding to the non-altered triacylglycerols.

Results obtained with various samples have shown that oligomeric compounds (triacylglycerol dimers and polymers) constitute the main fraction amongst the different groups of altered compounds formed during frying, generally representing more than 50% of total polar compounds, and their levels have had a good correlation with those determined for total polar compounds (Gere, 1982; Perrin et al., 1985; Masson et al., 1997).

Values of total polar compounds of 25% and of polymeric triacylglycerols of 10 or 16% have been established in different regulations as the maximum limit for rejection of the frying fat or oil (Tasioula-Margari et al., 1996; Bastida and Sánchez-Muñiz, 2002).

Considering that the frying process is influenced by many variables, including the degree of unsaturation of the oil, the use of partially hydrogenated fats is a solution to increase the stability of frying oils, reducing the formation of degradation compounds.

The presence of natural or added minor compounds, such as tocopherols, also influences the formation of degradation compounds. Tocopherols are the most important natural antioxidants present in vegetable oils (Kamal-Eldin and Appelqvist, 1996). At low temperatures, the antioxidant activity of tocopherols has been ascribed to the transfer of their phenolic hydrogen to a peroxyl radical, leading to termination reactions that yield non-radical oxidation products (Verleyen et al., 2001). At high temperatures, their mode of action is not so clear.

Gertz et al. (2000) observed that non-refined oils proved to have better stability at elevated temperatures than refined oils, showing that the stability of vegetable oils at frying temperatures is a function of more than just the fatty acid composition.

There are a number of studies that evaluate the performance of oils submitted to thermal oxidation, which is a process similar to frying, but without the presence of food. However, very few have evaluated the performance of partially hydrogenated oils submitted to thermal oxidation, verifying the influence of the presence of tocopherols on their stability and the relation to iodine value.

The present study aims to know the behavior of partially hydrogenated soybean oils, with and without their natural tocopherols, when submitted to high temperatures. In particular, the formation of polymerization compounds and the loss of tocopherol were studied.

2. EXPERIMENTAL PART

2.1. Samples

Refined and partially hydrogenated soybean oils with iodine values of approximately 130 and 60 were kindly supplied by Cargill Agrícola S.A. (Mairinque, Brazil). Intermediate iodine value samples were prepared by blending.

2.2. Sample characterization

The following AOCS or IUPAC Official Methods were used to characterize the samples: Iodine Value (Recommended Practice AOCS Cd 1c-85, 1993), Oxidative Stability (AOCS Method Cd 12b-92, 1993, using Rancimat equipment at 110°C), Free Fatty Acids (AOCS Method Ca 5a-40, 1996), Peroxide Value (AOCS Method Cd 8b-90, 1996), Smoke Point (AOCS Method Cc 9a-48, 1993), Fatty Acid

Composition (AOCS Method Ce 1-62, 1993) and Tocopherols (IUPAC 2.432, 1992).

2.3. Aluminium oxide treatment

A portion of each sample was treated to remove originally present tocopherols. This stripping procedure was carried out as described by Yoshida et al. (1992), by passing 50 – 100 g of oil through a column with approximately double this amount of activated aluminium oxide (Al_2O_3: aluminium oxide 90, standardized for column chromatographic adsorption analyses, acc. to Brockmann, Merck, item n° 1.01097.1000). Aluminium oxide was activated in an oven at 200°C for at least 4 hours. After this treatment, each sample had its stripped or treated counterpart.

2.4. Thermal oxidation

8 ± 0.01 g of each sample were weighed in Rancimat tubes and inserted in the heating block previously heated to 180 1°C, following the procedure described by Barrera-Arellano et al. (1997). Two samples of approximately 50 mg were collected after 2, 5, 8 and 10 hours heating and kept at –30°C until analyses.

Rancimat instructions were carefully observed for glassware cleaning. During heating, the tubes were left open and no bubbling of air was applied.

2.5. Analysis of thermally oxidised samples

Dimers and polymers were quantitated directly in the oil samples, using high performance size-exclusion chromatography (HPSEC), according to Dobarganes et al. (1999). Conditions applied for HPSEC were as follows: a Waters 510 HPLC pump and a Rheodyne 7725i injector with a 10 m sample loop (Waters Associates, Milford, MA, USA), a Merck L-7490 refractive index detector (Merck, Darmstadt, Germany) and a Hewlett-Packard HP 3390A integrator (Hewlett-Packard, Pittsburgh, PA, USA) were used. Two Ultrastyragel columns (Waters Associates, Milford, MA, USA), 100 and 500 Å, connected in series, were used. The columns were 25 cm long x 0.77 cm inner diameter, packed with a porous, highly cross-linked styrenedivinylbenzene copolymer (<10 μm). High performance liquid chromatography grade tetrahydrofuran was used as mobile phase, with a flow rate of 1 mL/min. Sample solutions of about 50 mg of oil/mL tetrahydrofuran were prepared for analyses.

Tocopherols were determined by high performance liquid chromatography (HPLC), according to the IUPAC Standard Method 2.432 (IUPAC, 1992). Conditions applied for HPLC were as follows: a Waters 600 HPLC pump with a 20 L

sample loop or a Waters Model M45 Solvent Delivery System (Waters Associates, Milford, MA, USA) was used. A LiChrosorb SI 60 (250 x 4 mm) column packed with silica (average particle size of approximately 5 m) (Merck, Darmstadt, Germany) was used. A Hewlett-Packard 1046A programmable fluorescence detector (290 – 330 nm) and a Hewlett-Packard HP 3390A integrator (Hewlett-Packard, Pittsburgh, PA, USA) or Merck-Hitachi D2500 chromato-integrator were used (Merck, Darmstadt, Germany). Oil samples (approximately 50 mg) were dissolved in 1 mL n-hexane. Mobile phase was n-hexane:isopropanol (99:1), with a flow rate of 1 mL/min.

3. RESULTS AND DISCUSSION

Physicochemical characteristics of soybean oil and partially hydrogenated soybean fats are shown in Table I. It can be observed that oxidative stability was iodine value dependent – the lower the iodine value, the higher the stability. All other analytical indices were within expected ranges for refined fats and oils.

Table II shows the fatty acid composition of soybean oil and partially hydrogenated soybean fats. The results clearly show the effect of hydrogenation on the simultaneous reduction of iodine value and of the more unsaturated fatty acids (linolenic, C18:3, and linoleic, C18:2), with a concomitant increase of the monounsaturated and saturated fatty acids (oleic, C18:1, and stearic, C18:0, respectively).

The determination of tocopherols in soybean oil and partially hydrogenated soybean fats showed approximately the same concentration and composition in all samples, thus indicating that hydrogenation does not destroy tocopherols, as already described by Sonntag (1979). Ranges found in samples were 1237 – 1351 mg/kg total tocopherols, 200 – 218 mg/kg alpha-tocopherol, 29 –

34 mg/kg beta-tocopherol, 841 – 931 mg/kg gamma-tocopherol and 157 – 179 mg/kg delta-tocopherol.

The absence of tocopherols in aluminium oxide treated samples demonstrated the efficacy of the procedure in their removal. As expected, a drastic reduction in oxidative stability was observed for tocopherol-stripped samples (Table III). Barrera-Arellano et al. (2002), working with 6 different vegetable oils, including soybean oil, applied the same stripping procedure and obtained comparable values for natural and antioxidant-stripped soybean oil. In both series (original samples and aluminium oxide treated samples), stability increased exponentially as the iodine value decreased. Interestingly, the efficiency of natural tocopherols (ratio between induction times for original and tocopherol-stripped samples) ranged between 6.6 and 13.1 and increased with the degree of unsaturation, suggesting a loss of efficiency of tocopherols and, consequently, a major influence of fatty acid composition in the more hydrogenated samples.

The oxidative stability of Soybean 60 was particularly high, but this is due to its high degree of hydrogenation and the significant quantities of tocopherols present. High oxidative stability values were also observed by Barrera-Arellano et al. (2002) for natural olive oil (118 h) and natural palm oil (43 h), probably attributable to the natural polyphenols of the former and to the natural tocotrienols of the latter.

Table IV shows the evolution of dimers and polymers in soybean oil and fat samples, during 10 hours under thermal oxidation conditions. In the first place, in this study, aluminium oxide treated samples, without their original tocopherols, showed greater degradation than their original counterparts, demonstrating the importance of tocopherols in retarding thermal degradation. Andrikopoulos et al. (2002) also noted that the oil fatty acids were

Table I
Physicochemical characteristics of soybean oil and partially hydrogenated soybean fats

	Soybean 60	Soybean 75	Soybean 95	Soybean 115	Soybean 130
Iodine value	63.35	73.49	94.94	113.69	128.94
Oxidative stability (h)	192.10	56.50	20.40	13.00	14.00
Free fatty acids (% oleic acid)	0.05	0.05	0.05	0.05	0.05
Peroxide value (meq/kg)	0.47	0.43	0.77	0.51	1.19
Smoke point (°C)	216	213	210	210	210

The number included in the name of the sample indicates its approximate iodine value (IV); e.g., Soybean 60 has an approximate IV of 60.

Table II

Fatty acid composition of soybean oil and partially hydrogenated soybean fats

Fatty acids	Soybean 60	Soybean 75	Soybean 95	Soybean 115	Soybean 130
C 14:0	0.1	0.1	0.1	0.1	0.1
C 16:0	11.9	11.2	11.4	11.2	11.0
C 18:0	17.8	13.1	11.2	5.4	3.6
C 18:1	66.0	64.2	46.3	35.1	24.0
C 18:2	3.1	9.6	27.3	42.3	53.7
C 18:3	-	0.5	3.1	4.7	6.6
C 20:0	0.5	0.6	-	-	-
C 20:1	-	-	-	0.4	0.2
C 22:0	0.4	0.5	0.5	0.5	0.5
C 24:0	0.1	0.2	0.1	0.2	0.2
Saturated	30.8	25.7	23.3	17.4	15.4
Monounsaturated	66.0	64.2	46.3	35.5	24.2
Polyunsaturated	3.1	10.1	30.4	47.0	60.3

The number included in the name of the sample indicates its approximate iodine value (IV); e.g., Soybean 60 has an approximate IV of 60.

Table III

Oxidative stability in hours (Rancimat, 110°C) of soybean oil and partially hydrogenated soybean fats, with and without aluminium oxide treatment

	Soybean 60	Soybean 75	Soybean 95	Soybean 115	Soybean 130
OR	192.10	56.50	20.40	13.00	14.00
TR	29.20	7.40	1.80	1.10	1.07

OR = original, TR = treated with aluminium oxide to remove tocopherols
The number included in the name of the sample indicates its approximate iodine value (IV); e.g., Soybean 60 has an approximate IV of 60.

effectively protected from oxidation by the natural antioxidants. Secondly, the relation with iodine value was also defined – in general, the higher the iodine value, the greater the thermal degradation (more oligomeric compounds formed) after 10 h. (An exception was the original sample of Soybean 75). However, the differences were lower than expected, considering the enormous differences in oxidative stabilities shown in Table III. In the study by Barrera-Arellano et al. (2002), polymerization at high temperature did not reflect large differences in oxidative stability, as only small differences were found in polymer formation when considering the wide variation in the degree of unsaturation of the oils assayed. Results were in agreement with those reported for used frying fats and oils where differences in unsaturation degree were translated into low differences in degradation (Márquez-Ruiz et al., 1995; Warner et al., 1997), although in this study the results are especially valuable because the original samples only differ in the degree of unsaturation.

It is interesting to note that among the original (OR) samples (with tocopherols) the difference in polymerization degree after 10 h was greater than among treated (TR) samples. This can be explained

Table IV
**Evolution of dimers and polymers (%) in soybean oil and partially hydrogenated soybean fats, with
and without aluminium oxide treatment, submitted to thermal oxidation conditions**

Time (h)	Soybean 60		Soybean 75		Soybean 95		Soybean 115		Soybean 130	
	OR	TR	OR	TR	OR	TR	OR	TR	OR	TR
0	0.1	0.1	0.1	0.1	0.1	0.1	0.4	0.3	0.4	0.3
2	0.8	2.4	1.5	2.9	3.2	2.6	4.1	3.5	4.3	4.1
5	3.4	6.3	3.6	6.7	6.1	6.6	8.0	8.3	9.1	9.6
8	5.5	9.8	5.5	10.4	9.4	10.2	11.8	12.9	13.1	14.3
10	8.0	11.6	6.9	12.5	11.1	12.5	14.0	15.5	15.5	17.2

OR = original, TR = treated with aluminium oxide to remove tocopherols
The number included in the name of the sample indicates its approximate iodine value (IV); e.g., Soybean 60 has an approximate IV of 60.

by the higher polymerization degree of treated Soybean 60, without the protection of tocopherols, and by the similar polymerization degrees of original and treated Soybean 130 (in the case of the more unsaturated samples, more prone to oxidation, it seems that the tocopherol content was not so effective in retarding the formation of polymers).

Considering that polymers increase linearly in time for each sample during thermal oxidation, the linear increase of polymers in original Soybean 60 at 180°C was 0.79%/hour and for treated Soybean 60 at 180°C it was 1.15%/h. For original Soybean 130, the linear increase of polymers was 1.51%/h and for treated Soybean 130 it was 1.69%/h. Verleyen et al. (2001) found values of 1.07%/h at 200°C and 2.3%/h at 225°C for unsaturated triacylglycerol levels (in model systems ranging between triolein and tripalmitin) and 1000 mg/kg initial concentration of -tocopherol.

Oils with more than 10% dimers plus polymers should be discarded according to the regulations of some countries (Tasioula-Margari et al., 1996; Bastida and Sánchez-Muñiz, 2002). In this study, polymerization levels below 10% (acceptable oils) after 10 hours at 180°C were found only for the more saturated samples (Soybean 60 and Soybean 75), with their original tocopherols. These samples had higher contents of stearic and oleic acids, but lower levels of linoleic and linolenic acids, more susceptible to oxidation.

In Figure 1, the degradation of individual tocopherols in soybean oil and fat samples, submitted to thermal oxidation conditions, can be observed. Alpha and γ-tocopherols presented greater degradation rates than β and δ-tocopherols. In model systems with added tocopherols, α-tocopherol was less stable than δ-tocopherol, while β and γ-tocopherols degraded at an intermediate rate (Barrera-Arellano et al., 1999). Verleyen et al. (2001)

also noted a very fast degradation of α-tocopherol. However, Masson et al. (2001) reported a greater loss of δ-tocopherol (43%) than of γ-tocopherols (30%) in oil extracted from potato crisps after frying.

In this study, samples with higher iodine values (those that presented greater thermal degradation) retained their tocopherols longer than those with lower iodine values. After 10 h of heating, significant amounts of tocopherols remained in the more unsaturated samples, while the more saturated fats were already unprotected, under the conditions used. Similar observations were made by Barrera-Arellano et al. (2002) for polyunsaturated and monounsaturated oils, where levels of 30–52% tocopherols remained in polyunsaturated oils and monounsaturated oils became unprotected at low levels of polymerisation.

Observing Figure 1 (c), where the degradation of γ-tocopherol, the major tocopherol in soybean fats and oils, is shown, residual concentrations of 27.3, 16.6, 11.8, 0 and 0% were found for Soybean 130, 115, 95, 75 and 60, respectively. The same pattern was followed by the other tocopherols. This behavior, where fats and oils with high unsaturation degrade faster but retain their tocopherols, was already described by Barrera-Arellano et al. (1999) (for α-tocopherol, but not for δ-tocopherol) and Verleyen et al. (2001), in triacylglycerol model systems; by Wilke de Souza (2001), in animal fats of different unsaturation degrees; and by Jorge et al. (1996a, 1996b), working with sunflower oil and high-oleic sunflower oil. An explanation for this behavior was given by Verleyen et al. (2001, 2002), observing that the rate of α-tocopherol oxidation decreased by competitive oxidation of unsaturated triacylglycerols, suggesting a non-selective oxidation of unsaturated fatty acyls and α-tocopherol by highly reactive alkoxyl and hydroxyl radicals generated by decomposition of hydroperoxides.
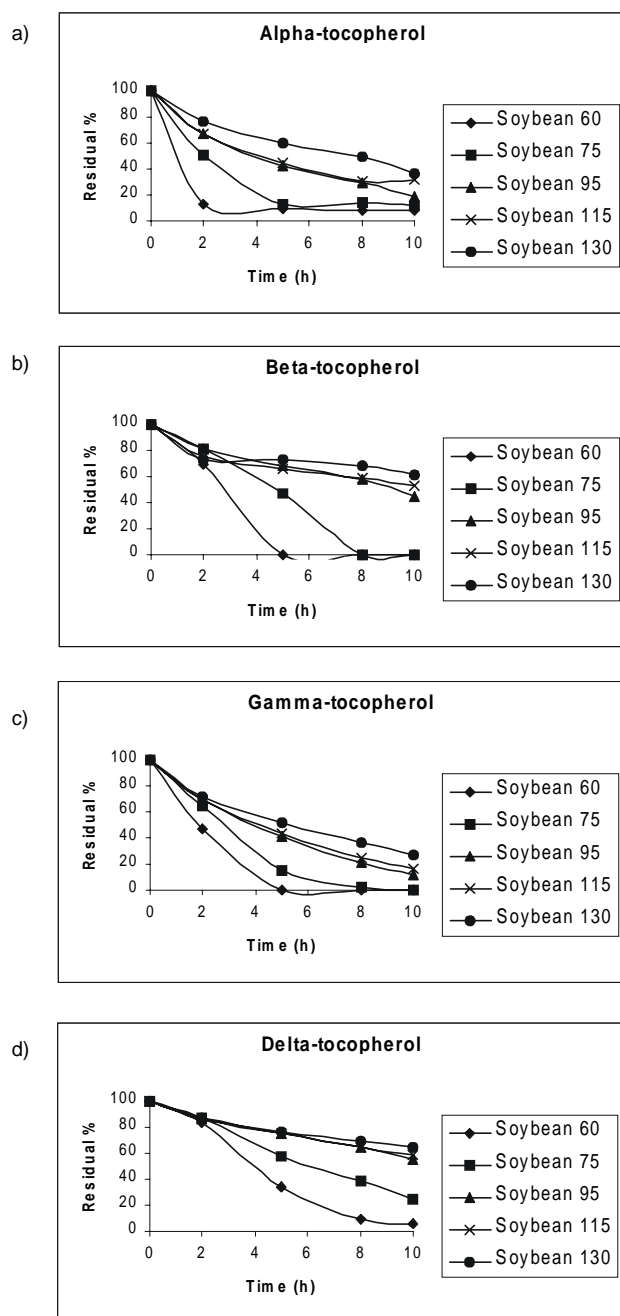
a)

Alpha-tocopherol

Residual %

Soybean 60
Soybean 75
Soybean 95
Soybean 115
Soybean 130

Time (h)

b)

Beta-tocopherol

Residual %

Soybean 60
Soybean 75
Soybean 95
Soybean 115
Soybean 130

Time (h)

c)

Gamma-tocopherol

Residual %

Soybean 60
Soybean 75
Soybean 95
Soybean 115
Soybean 130

Time (h)

d)

Delta-tocopherol

Residual %

Soybean 60
Soybean 75
Soybean 95
Soybean 115
Soybean 130

Time (h)

Figure 1
Evolution of tocopherols (residual %) in original soybean
oil and partially hydrogenated soybean fats submitted to thermal
oxidation conditions: a) alpha-tocopherol, b) beta-tocopherol,
c) gamma-tocopherol and d) delta-tocopherol. The number
included in the name of the sample indicates its approximate
iodine value (IV); e.g., Soybean 60 has an approximate IV of 60.

The different rates of tocopherol losses might also justify some unexpected results. For example, in the case of the less unsaturated fat (Soybean 60), tocopherols practically disappeared after 8 hours, which could explain the high degradation undergone between 8 and 10 hours, as compared to Soybean

75, that still contained around 25% of δ-tocopherol after 8 hours.

Overall, these results suggest the complexity of degradation at high temperatures. In opposition to what occurs at low or medium temperatures, substrates of low iodine values may be unprotected from natural antioxidants very rapidly and at low levels of polymerization. It is important to take this fact into account when considering the shelf-life of fried products where it might be interesting to have tocopherols present to retard oxidation.

4. CONCLUSIONS

From the results obtained, the following conclusions can be drawn:

1. Thermal degradation depends on the iodine value of refined and partially hydrogenated soybean oils, although differences in susceptibility to polymerization were much lower than those expected from differences in susceptibility to oxidation.

2. Natural tocopherols contributed to decrease polymerisation in refined and partially hydrogenated soybean oils.

3. Tocopherols were lost at a faster rate as the degree of unsaturation decreased and δ-tocopherol was the most stable tocopherol.

ACKNOWLEDGEMENTS

BIBLIOGRAPHY

Andrikopoulos N.K., Dedoussis G.V.Z., Falirea A., Kalogeropoulos N., Hatzinikola H.S. 2002. Deterioration of natural antioxidant species of vegetable edible oils during the domestic deep-frying and pan-frying of potatoes. *Int. J. Food Sci. Nutr.* **53**, 351-363.

AOCS – American Oil Chemists' Society. 1993, including 1996 update. *Official methods and recommended practices of the American Oil Chemists' Society*, 4th ed., AOCS, Champaign.

Barrera-Arellano D., Márquez-Ruiz G., Dobarganes M.C. 1997. A simple procedure to evaluate the performance of fats and oils at frying temperatures. *Grasas y Aceites* **48**, 231-235.

Barrera-Arellano D., Ruiz-Méndez M.V., Márquez-Ruiz G., Dobarganes M.C. 1999. Loss of tocopherols and formation of degradation compounds in triacylglycerol model systems heated at high temperature. *J. Sci. Food Agric.* **79**, 1-6.

Barrera-Arellano D., Ruiz-Méndez V., Velasco J., Márquez-Ruiz G., Dobarganes C. 2002. Loss of tocopherols and formation of degradation compounds at frying temperatures in oils differing in degree of

unsaturation and natural antioxidant content. *J. Sci. Food Agric.* **82**, 1696-1702.

Bastida S., Sánchez-Muñiz F.J. 2001. Thermal oxidation of olive oil, sunflower oil and a mix of both oils during forty discontinuous domestic fryings of different foods. *Food Sci. Technol. Int.* **7**, 15-21.

Bastida S., Sánchez-Muniz F.J. 2002. Polar content versus TAG oilgomer content in the frying-life assessment of monounsaturated and polyunsaturated oils used in deep-frying. *J. Am. Oil Chem. Soc.* **79**, 447-451.

Dobarganes M.C., Márquez-Ruiz G., Berdeaux O., Velasco J. 1999. Determination of oxidation compounds and oligomers by chromatographic techniques in Boskou D., Elmadfa I. (Eds.) *Frying of Food: Oxidation, Nutrient and Non-Nutrient Antioxidants,Biologically Active Compounds and High Temperatures*, p.143-161, , Technomic Publishing Co., Inc., Lancaster, Pennsylvania.

Gere A. 1982. Studies of the changes in edible fats during heating and frying. *Die Nahrung* **26**, 923-932.

Gertz C., Klostermann S., Kochhar S.P. 2000. Testing and comparing oxidative stability of vegetable oils and fats at frying temperature. *Eur. J. Lipid Sci. Technol.* **102**, 543-551.

IUPAC – International Union of Pure and Applied Chemistry 1992. Method 2.432 in *Standard Methods for the Analysis of Oils, Fats and Derivatives.* 7th edition, Pergamon Press, Oxford.

Jorge N., Márquez-Ruiz G., Martín-Polvillo M., Ruiz-Méndez M.V., Dobarganes M.C. 1996a. Influence of dimethylpolysiloxane addition to frying oils: performance of sunflower oil in discontinuous and continuous laboratory frying. *Grasas y Aceites* **47**, 20-25.

Jorge N., Márquez-Ruiz G., Martín-Polvillo M., Ruiz-Méndez M.V., Dobarganes M.C. 1996b. Influence of dimethylpolysiloxane addition to edible oils: dependence of the main variables of the frying process. *Grasas y Aceites* **47**, 14-19.

Kamal-Eldin A., Appelqvist, L. 1996. The chemistry and antioxidant properties of tocopherols and tocotrienols. *Lipids* **31**, 671-701.

Márquez-Ruiz G., Tasioula-Margari, M., Dobarganes, M.C. 1995. Quantitation and distribution of altered fatty acids in frying fats. *J. Am. Oil Chem. Soc.* **72**, 1171-1176.

Masson L., Robert P., Romero N., Izaurieta M., Valenzuela S., Ortiz J., Dobarganes, M.C. 1997. Comportamiento de aceites poliinsaturados en la preparación de patatas fritas para consumo inmediato: formación de nuevos compuestos y comparación de métodos analíticos. *Grasas y Aceites* **48**, 273-281.

Masson L., Urra C., Izaurieta M., Ortiz J., Robert P., Romero N., Wittig, E. 2001. Stability of potato crisps subjected to several conditions of storage. *Grasas y Aceites* **52**, 175-183.

Pérez-Camino M.C., Márquez-Ruiz G., Salgado Raposo A., Dobarganes M.C. 1988. Alteración de grasas usadas en fritura. III. Correlación entre índices analíticos y métodos de evaluación directa de compuestos de degradación. *Grasas y Aceites* **39**, 72-76.

Perrin J.L., Perfetti P., Dimitriades C., Naudet M. 1985. Étude analytique approfondie d'huiles chauffées. I. Techniques analytiques et essais préliminaires. *Rev. Fr. Corps Gras* **32**, 151-158.

Rossell J.B. 1998. Industrial frying process. *Grasas y Aceites* **49**, 282-295.

Sonntag N.O.V. 1979. Structure and composition of fats and oils in Swern, D. (Ed.) *Bailey's Industrial Oil and Fat Products*, Vol. 1, 4th ed., p. 1-98, John Wiley & Sons, New York.

Tasioula-Margari M., Márquez-Ruiz G., Dobarganes M.C. 1996. Fractionation of oligomeric triacylglycerides and the relation to rejection limits for used frying oils. *J. Am. Oil Chem. Soc.* **73**, 1579-1584.

Verleyen T., Kamal-Eldin A., Dobarganes C., Verhe R., Dewettinck K., Huyghebaert A. 2001. Modeling of -tocopherol loss and oxidation products formed during thermoxidation in triolein and tripalmitin mixtures. *Lipids* **36**, 719-726.

Verleyen T., Kamal-Eldin A., Mozuraityte R., Verhe R., Dewettinck K., Huyghebaert A., De Greyt W. 2002. Oxidation at elevated temperatures: competition between alpha-tocopherol and unsaturated triacylglycerols. *Eur. J. Lipid Sci. Technol.* **104**, 228-233.

Warner K. 1997. Chemistry of frying fats in Akoh, C.C., Min, D. B. (Eds.) *Food Lipids: Chemistry, Nutrition and Biotechnology*, p. 167-180, Marcel Dekker, Inc., New York.

Warner K., Orr P., Glynn, M. 1997. Effect of fatty acid composition of oils on flavor and stability of fried foods. *J. Am. Oil Chem. Soc.* **74**, 347-356.

Wilke de Souza S.M. 2001. *Termoxidação de gorduras animais*. 79p. Thesis (Master's Degree in Food Technology) – Faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas, São Paulo, Brazil.

Yoshida H., Kondo I., Kajimoto G. 1992. Participation of free fatty acids in the oxidation of purified soybean oil during microwave heating. *J. Am. Oil Chem. Soc.* **69**, 1136-1140.