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Effects of the type of frying with culinary fat and refrigerated storage on lipid oxidation and colour of fried pork loin chops

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Abstract

The effects of different types of culinary frying fats and oils (olive oil -OO-, sunflower oil -SO-, butter -BT- and pig lard -PL-) were studied in relation to lipid oxidation and instrumental colour in fried pork loin chops during 10 days of refrigerated storage. At day 0, pork loin chops fried in butter showed significantly lower values of TBARS (0.37 mg MDA/kg, $p < 0.05$) than pork loin chops fried in the oils/fats (OO = 0.57 mg MDA/kg, SO = 0.55 mg MDA/kg, PL = 0.61 mg MDA/kg, $p < 0.05$). After 10 days of refrigerated storage, the highest TBARS values were found in BT (2.06 mg MDA/kg), while the lowest one was found in OO (0.91 mg MDA/kg.). At day 10, SO and PL showed intermediate values for BT and OO (SO = 1.71 mg MDA/kg, PL = 1.74 mg MDA/kg, $p < 0.05$). Pork loin chops showed a progressive discolouration during 10 days of refrigerated storage. Parameters of instrumental colour values (L^*, a^*, b^*, c^*) tended to decrease during the storage period, while $h°$ values tended to increase. High negative correlation was observed between methanol-extracted coloured materials and TBARS values at 10 days (Pearson's Correlation = −0.783, $p < 0.01$), which is indicative of a possible antioxidant activity of Maillard reaction products (MRPs). Lipid oxidation and colour of fried and refrigerated meat were possibly influenced by changes in fatty acid profiles of meat, incorporation of natural antioxidants (proceeding from vegetable oils) and antioxidant activity of MRPs formed during the frying period.

Keywords: Frying culinary fat; Meat; Colour; Lipid oxidation; Refrigeration

1. Introduction

Frying is a common and popular process, often utilized in the food industry due to its significant sales and vast quantity of fried products. From the consumers standpoint, fried food palatability is related to unique sensory characteristics, including flavour, texture and appearance (Saguy & Dana, 2003).

In recent years, the great increase in catering and restaurant sectors shows the economic importance of fried food, mainly fast food enterprises. For example, in 1970 Americans spent $6000 million on fast foods. In 2000, this figure grew to $110,000 million (Saguy & Dana, 2003). Reasons for the rising consumption of fried foods are related to the improved sensory characteristics and their fast and easy preparation (Romero, Cuesta, & Sánchez-Muniz, 2001; Varela & Ruiz-Rosso, 2000).

Frying modifies food properties due: (i) to induction of water loss, (ii) to stimulation of thermo-oxidation reactions caused by the contact of frying oils heated at high temperatures with the meat surface, (iii) to change of the colour to brown and (iv) to modify lipid profile. In reference to the latter point, the type of fat or oil used has a great influence on final product characteristics. In Spain, food is fried mainly in olive oil, sunflower oil and mixes of both, but other countries use other fats, such as butter or pig lard (Bastida & Sánchez-Muniz, 2001). Fats/oils have different compositions of fatty acids, antioxidant compounds and pigments. During frying, the fat or oil acts as a heat transfer medium and becomes an important ingredient of the fried food because water loss, as well as penetration of oil into the food, takes

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place (Moreiras-Varela, Ruiz-Roso, & Varela, 1988). These interactions depend on both initial characteristics of culinary fat and food and frying procedure characteristics (Guillaumin, 1988). The use of different oils or fats modifies the food characteristics because part of them remains in the fried food, causing a modification of lipid profile and aroma (Ramírez & Cava, 2004; Sánchez-Muniz, Viejo, & Medina, 1992). During frying, minority compounds, such as carotenes, phytosterols and tocopherols, are incorporated in the food (Cuesta & Sánchez-Muniz, 2001).

Sometimes, cooked meat is refrigerated before it is consumed. Lipid oxidation is the principal cause of deterioration of the quality of cooked meats during storage (Pearson, Love, & Shortland, 1977). Lipid oxidation is much faster in cooked meat than in fresh meat, due to the fact that cooking induces an acceleration of the oxidative processes as a result of the high temperatures reached during processing (Kingston, Monahan, Buckley, & Lynch, 1998), the destruction of cellular structures, that allows the interaction between polyunsaturated fatty acids and prooxidants (Reineccius, 1979; Rhee, 1988) and the release of non-heme iron (Kristensen & Andersen, 1997; Kristensen & Purslow, 2001). The colorimetric determination of TBARS has long been accepted as an indicator of food quality deterioration in terms of lipid oxidation (Spanier, Vincent Edwards, & Dupuy, 1988). The TBARS test is very effective for assessing the lipid oxidation that is associated with the development of undesirable flavours (warmed-over-flavour) in refrigerated cooked meat (Byrne, Bredie, Bak, Bertelsen, Martens, & Martens, 2001; Poste, Willemont, Butler, & Patterson, 1986; Spanier et al., 1988; St. Angelo, Crippen, Dupuy, & James,. 1990). Additionally, those factors which affect lipid oxidation are closely related to the stability of meat colour. Numerous papers have described a close relationship between the development of lipid oxidation and the discolouration of meat (Faustman & Cansens, 1990; OGrady et al., 1996; O'Grady, Monahan, Bailey, Allen, Buckley, & Keane, 1998; Yin & Faustman, 1993).

Frying modifies the colour surface as a result of the development of Maillard reactions which are responsible for browning in meat containing reducing sugars and free amino groups, which are produced when meat is cooked at high temperature (Hodge, 1953). In fried food, the development of these reactions is favoured by high temperatures, over 110 °C, reached when food makes contact with frying fat and the dehydration of the outer layer (Whitfield, 1992). Bailey (1988) showed that Maillard reaction products (MRPs) could act as antioxidants during refrigerated storage of cooked meat.

The objective of this work was to evaluate the instrumental colour changes and lipid oxidation in pork loin chops fried in different culinary fats/oils during refrigerated storage.

2. Materials and methods

2.1. Materials

Olive oil, with an acidity value of 0.4 and with a content of α-tocopherol of 20 mg/100g, refined sunflower oil with an acidity value of 0.2 and with a content of α-tocopherol of 60 mg/100 g, butter and pig lard were purchased at a local store. The choice of such culinary fats was based on both their fat composition (olive oil being high in monounsaturated fatty acids, sunflower oil being high in polyunsaturated fatty acids, butter being high in saturated fatty acids, and pig lard being high in mono and polyunsaturated fatty acids) (Table 1) and common culinary fats used for different gastronomic cultures. Pork loin (m. *Longissimus dorsi*) was also purchased at a local store. Loin was sliced using a slicing machine, yielding 15-mm thickness chops.

2.2. Methods

2.2.1. Performance of frying and refrigerated storage conditions

About 80 g of pork loin (2 chops × 5 replications) were fried in olive oil, sunflower oil, butter and pig lard. Frying was performed on an electric stove at 160 °C in domestic stainless steel-teflon coated pans of 2l-l capacity. Culinary fats were used once, with the food/oil ratio being 20 g/500 ml. The frying lasted 2 min, turned round after 1 min of frying. Oil and food-core temperatures were checked using a quartz electronic thermometer during frying. Once fried, samples were drained for about 2 min and dried in a paper towel to eliminate remains of oils on the loin slice surface. Once fried, samples were placed on Styrofoam meat trays and over-wrapped with PVC oxygen-permeable films and stored at +4 °C for 10 days under fluorescent light.

2.2.2. Fatty acid profile determination

Fatty acid methyl esters were prepared by transesterification, using methanol in the presence of sulphuric acid (5% of sulphuric acid in methanol) following the method of Cava et al. (1997). Fatty acid methyl esters (FAMEs) were analysed using a Hewlett Packard, model HP-5890A, gas chromatograph, equipped with a flame ionization detector (FID). The derivatives were separated on a semi-capillary column (Hewlett Packard FFAP-TPA fused-silica column, 30 m length, 0.53 mm internal diameter and 1.0 μm film thickness). The injector and the detector temperatures were held at 230 °C. Column oven temperature was maintained at 220 °C. The flow rate of the carrier gas (N_2) was set at 1.8 ml/min. Identification of FAMEs was based on retention times of reference compounds (Sigma). Fatty acid composition was expressed as percent of total fatty acid methyl esters.

Table 1
Major fatty acid composition of olive oil, sunflower oil, butter and pig lard prior to and after frying pork loin chops (Fatty acid methyl ester, FAMES as of total FAME)

Culinary fat	OO		SO		BT		PL	
	Before	After	Before	After	Before	After	Before	After
C12	0.0	0.0	0.0	0.0	3.7	3.3	0.0	0.1
C14	0.0	0.0	0.1	0.1	13.4	12.1	1.2	1.2
C16	10.1	9.9	6.3	6.3	39.5	34.6	23.0	23.5
C17	0.0	0.2	0.0	0.0	0.7	0.6	0.5	0.5
C18	3.3	3.4	3.8	4.0	11.0	13.3	12.6	12.9
C20	0.4	0.5	0.3	0.3	0	0.2	0.2	0.2
SFA	13.8	14.0	10.5	10.7	68.2	64.1	37.5	38.4
C16:1	0.7	0.8	0.2	0.1	3.5	2.3	2.6	2.7
C17:1	0.1	0.1	0.0	0.0	0.4	0.4	0.4	0.4
C18:1	78.7	78.5	30.5	28.0	27.4	30.1	42.1	42.4
C20:1	0.3	0.3	0.2	0.3	0.2	0.3	1.0	0.1
MUFA	79.8	79.7	30.9	28.4	31.5	33.1	46.1	45.6
C18:2	5.6	5.6	58.6	60.7	3.7	2.1	14.6	14.6
C18:3	0.6	0.6	0.1	0.1	0.2	0.5	1.0	1.0
C20:2	0.1	0.1	0.0	0.0	0	0.0	0.6	0.0
C20:4	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.3
PUFA	6.3	6.3	58.7	60.8	3.9	2.7	16.2	15.9
$n-6$	5.7	5.7	58.6	60.7	3.8	2.2	15.2	14.9
$n-3$	0.6	0.6	0.1	0.1	0.2	0.5	1.0	1.0
$n-6/n-3$	9.5	9.5	586.0	607.0	18.9	4.4	15.2	14.9

OO: olive oil; SO: sunflower oil; BT: butter; PL: pig lard; SFA: saturated fatty acids (C12, C14, C16, C17, C18, C20); MUFA: monounsaturated fatty acids (C16:1, C17:1, C18:1, C20:1); PUFA: polyunsaturated fatty acids (C18:2, C18:3, C20:2, C20:4); $n-3$: $n-3$ fatty acids (C18:3); $n-6$: $n-6$ fatty acids (C18:2, C20:2; C20:4).

2.2.3. Extraction of coloured material

For extraction of coloured materials formed by frying, a protocol described by Fogliano, Monti, Musella, Randazzo, and Ritieni (1999) was followed. About 0.5 g of each sample was finely ground and placed in a glass tube. Four different solvents (4 ml) were used for colour extraction: water, methanol, ethanol and acetone. Tubes were hermetically closed and placed in an orbital shaker. After 1 h, tubes were centrifuged at 5000*g* for 10 min. Pellets were discarded and the absorbances of supernatants at 420 nm were recorded.

2.2.4. Lipid oxidation

Lipid oxidation was assessed, in duplicate, by the 2-thiobarbituric acid (TBA) method of Salih, Smith, Price, and Dawson (1987), using 2 g of meat samples. TBARS values were calculated from a standard curve of malondialdehyde and expressed as mg malondialdehyde kg^{-1} meat.

2.2.5. Instrumental colour

Colour measurements were taken immediately after opening the package (so as to prevent colour deterioration as a result of light and oxygen) in accordance with the recommendations on colour determination of the American Meat Science Association (Hunt et al., 1991). The CIELAB colour space was studied in accordance with Cassens et al. (1995). The following colour coordinates were determined: lightness (L^*), redness (a^*, red-green) and yellowness (b^*, yellow-blue). The colour parameters were determined using a Minolta CR-300 colorimeter (Minolta Camera Co., Osaka, Japan). Illuminant D65 was chosen and a 10° standard observer (Cassens et al., 1995). In addition, hue angle, which describes the hue or colour ($h°$) was calculated $[h° = \tan^{-1}(b^*/a^*)]$, as was the saturation index or chroma (c^*) $[c^* = (a^{*2} + b^{*2})^{0.5}]$, which describes the brightness or vividness of colour. Before use, the colorimeter was standardized using a white tile. The measurement was repeated on eight randomly selected locations on each loin slice and averaged for statistical analysis.

2.2.6. Data analysis

For the analysis of the effect of the type of culinary fat (olive oil, sunflower oil, butter or pig lard) on the absorbances, at 420 nm, of the coloured extracted material, an analysis of variance (ANOVA) was used. HSD Tukey's test was used when ANOVA found significant differences between treatments. In order to determine the effect of the type of culinary fat and the storage time on the evolution of lipid oxidation and instrumental colour coordinates, an analysis of variance (ANOVA), following the generalized linear model (GLM) for a 4 (treatments) × 4 (days of storage) with the interaction was used (SPSS, 1997). HSD Tukey's tests were used

when ANOVA found significant differences between treatments. The relationship between the absorbances of extracted coloured materials and TBARS values and instrumental colour coordinates at 0, 3, 7 and 10 days of refrigerated storage was evaluated using Pearson's correlation coefficients.

3. Results and discussion

3.1. Extracted coloured materials

Mean values of absorbances, at 420 nm, of extracted coloured materials, using different solvents (deionized water, methanol, ethanol and acetone) from loin chops fried in different culinary fats, are shown in Table 2.

No differences in the water- or ethanol-extracted coloured materials were found between treatments. Absorbances, at 420 nm, of methanol-extracted coloured materials were significantly higher in OO samples than in BT ones (OO = 0.096 vs BT = 0.052, $p < 0.05$). However, absorbances, at 420 nm, of acetone-extracted coloured materials were significantly higher in PL samples than in samples fried in the two vegetable oils – olive and sunflower oils – (PL = 0.063, OO = 0.004, SO = 0.002, $p < 0.05$). The degree of browning (usually measured via absorbance at 420 nm) is often used analytically to assess the extent to which the Maillard reaction has taken place in foods. Results revealed a different formation of coloured materials, as affected by the kind of culinary fat used for frying, that could be related to colour development and oxidative status of the fried samples. Numerous authors have described Maillard reaction products, responsible for browning, due to formation of brown melanoidins, and the development of heat-induced antioxidants in cooked meat (Bendinghaus & Ockerman, 1995; Hansen & Hemphill, 1984). Since no studies of effects of frying oils on colour materials extractable with different solvents have been reported, it is not possible to compare and discuss the results.

Table 3 shows the probability values of the 2-ways interaction ANOVA for TBARS and instrumental colour of pork loin chops fried in different culinary fats and stored at +4 °C for 0, 3, 7 and 10 days.

3.2. Lipid oxidation changes

ANOVA results for lipid oxidation (TBARS expressed as mg malondialdehyde (MDA)/kg meat) indicated significant differences due to the type of culinary frying fat used ($p = 0.000$) and storage time ($p = 0.000$); additionally a statistically significant interaction was found ($p = 0.005$) (Table 3). Changes in TBARS of pork loin chops fried in different culinary fats during refrigerated storage are shown in Fig. 1.

Pork loin chops fried in different culinary fats suffered great lipid oxidation changes during refrigerated storage. TBARS increased in all groups; however the increase in TBARS depended on the type of culinary fat ($p < 0.000$). In this sense, from day 0 to day 10, TBARS increased 1.6-, 3.1-, 5.6- and 2.9-fold in pork loin chops fried in olive oil, sunflower oil, butter and pig lard, respectively.

The Tukey's test, applied to the type of culinary fat, showed significant differences at days 0, 3 and 10 between groups. At day 0, BT samples showed significantly lower TBARS than samples fried in the other culinary fats (BT = 0.37 mg MDA/kg, OL = 0.57 mg MDA/kg, SO = 0.55 mg MDA/kg, PL = 0.61 mg MDA/kg, $p < 0.05$). After 10 days of refrigerated storage, BT samples showed the highest TBARS values (2.06 mg MDA/kg), while OO samples exhibited the lowest TBARS values (0.91 mg MDA/kg) and SO and PL samples showed intermediate TBARS values (SO = 1.71 mg MDA/kg, PL = 1.74 mg MDA/kg, $p < 0.05$).

These findings show a close relationship between the development of lipid oxidation and fatty acid composition and antioxidant content of each type of culinary fat.

Frying involves an exchange of fatty acids between the fat in the meat and the culinary fat used, causing an alteration of the fatty acid profiles of the meat, and tending to make the fat composition of meat similar to that of the frying culinary fat (Ramírez & Cava, 2004; Sánchez-Muniz et al., 1992). Furthermore, some minority compounds, such as α-tocopherol, present in vegetable oils (sunflower and olive oil), are taken up by the meat during frying.

Thus, oxidative changes in pork loin chops fried in the different culinary fats are greatly affected by factors

Table 2
Absorbance, at 420 nm, of coloured material extracted after 1 h using different solvents (deionized water, methanol, ethanol and acetone). Data are representative of five determinations

Solvents	Culinary fat				SEM	*p*-value
	OO	SO	BT	PL		
Deionized water	0.266	0.414	0.180	0.204	0.035	0.067
Methanol	0.096a	0.068ab	0.052b	0.082ab	0.006	0.038
Ethanol	0.032	0.044	0.050	0.072	0.006	0.075
Acetone	0.004b	0.002b	0.038ab	0.063a	0.008	0.016

OO: olive oil; SO: sunflower oil; BT: butter; PL: pig lard; a,b: Values are means of five determinations in homogenized samples of fried pork loin chops. Values in the same row bearing different letters are significantly different (Tukey test, $p < 0.05$).

Table 3
Results of the ANOVA for TBARS and instrumental colour (L^*, a^*, b^*, c^* and $h°$) of pork loin chops fried in different culinary fats and stored at +4 °C during 0, 3, 7 and 10 days

Variable	Source	SS	DF	MS	F	Significance
TBARS	Type of culinary fat	3.1197	3	1.0399	7.8351	0.000
	Storage	11.5826	3	3.8609	29.0894	0.000
	Interaction	3.5635	9	0.3959	2.9832	0.005
	Error	7.8307	59	0.1327		
L^*	Type of culinary fat	1302.0060	3	434.0020	25.4369	0.000
	Storage	58.3751	3	19.4584	1.1405	0.340
	Interaction	91.6204	9	10.1800	0.5967	0.795
	Error	1006.6520	59	17.0619		
a^*	Type of culinary fat	85.3287	3	28.4429	9.3091	0.000
	Storage	100.7898	3	33.5966	10.9959	0.000
	Interaction	30.2591	9	3.3621	1.1004	0.377
	Error	180.2669	59	3.0554		
b^*	Type of culinary fat	147.5652	3	49.1884	6.3824	0.001
	Storage	18.1776	3	6.0592	0.7862	0.506
	Interaction	63.5210	9	7.0579	0.9158	0.518
	Error	454.7071	59	7.7069		
c^*	Type of culinary fat	194.3806	3	64.7935	6.8080	0.001
	Storage	44.8488	3	14.9496	1.5708	0.206
	Interaction	84.2893	9	9.3655	0.9841	0.463
	Error	561.5148	59	9.5172		
$h°$	Type of culinary fat	208.6657	3	69.5552	9.5176	0.000
	Storage	415.4025	3	138.4675	18.9472	0.000
	Interaction	55.6844	9	6.1872	0.8466	0.577
	Error	431.1757	59	7.3081		

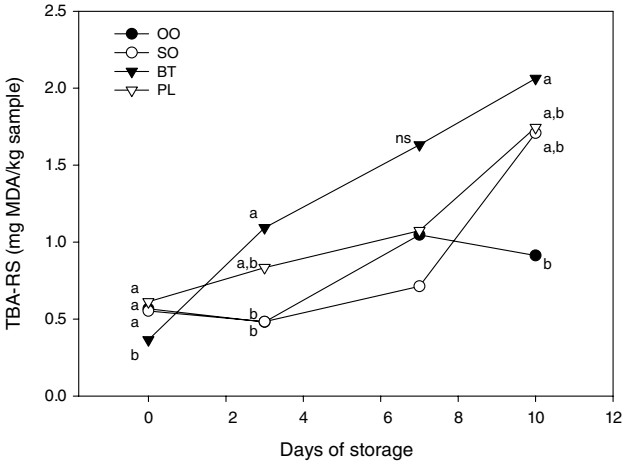

Fig. 1. Evolution of lipid oxidation in pork loin chops (*m. Longissimus dorsi*) fried in different culinary fats and stored at +4 °C (a,b: Different letters for the same day of refrigerated storage denote a statistical difference (Tukey test, $p < 0.05$); OO: olive oil; SO: sunflower oil; BT: butter; PL: pig lard).

related to the chemical composition of each culinary fat, associated with: (i) modification in the fatty acid profile and (ii) content of antioxidant compounds incorporated in the meat; furthermore there are other factors related to the frying process which lead to formation of heat-induced antioxidants, such as MRPs.

In a previous paper, Ramírez and Cava (2004) reported percentages of C18:1 $n-9$ of 59.1% and 39.5% in neutral lipids (NL) and free-fatty acid (FFA) fractions of OO samples. Additionally, OO samples exhibited high levels of MRPs, measured as absorbances at 420 nm of methanol-extracted coloured compounds ($Abs_{420\ nm}$: 0.096). In the case of SO samples, NL and FFA fractions showed higher percentages of linoleic acid (C18:2 $n-6$: 31.3% and 25.3% in NL and FFA fractions, respectively), thus the oxidative stability could be attributable to other factors dependent on frying media or frying process. The incorporation of antioxidants, mainly α-tocopherol, from oil, could contribute to the stabilization of lipids against oxidative deterioration. In this sense, Holland, Welch, Unwin, Buss, Paul, and Southgate (1991) described that fried foods, due to oil uptake, are enriched with considerable amounts of tocopherols. Taking into account α-tocopherol of vegetable oils (SO: 60 mg/100g vs OO: 20 mg/100g), the incorporation of this antioxidant could be expected to be higher in SO samples than in OO samples. Furthermore, the measurements of the absorbances at 420 nm of methanol-extracted coloured materials showed high values ($Abs_{420\ nm}$: 0.068). Both factors

could be responsible for the great oxidative stability, during storage, of SO samples even with a high content of the (highly susceptible to oxidation) polyunsaturated fatty acids.

PL samples presented oxidative stability similar to SO samples, attributable, in this case, to the high content of monounsaturated fatty acids (C18:1 $n-9$: 43.8% and 32.1% in NL and FFA, respectively) and saturated fatty acids (39.4% in NL) (Ramírez & Cava, 2004) with a high stability to oxidative deterioration, and to the antioxidant effect of heat-induced antioxidant formed during frying ($Abs_{420\ nm}$: 0.082, for methanol-extracted coloured materials).

Finally, at day 10, BT samples exhibited the highest TBARS values (2.06 mg MDA/kg), probably due to a poor incorporation of natural antioxidants and heat-induced antioxidant substance formation ($Abs_{420\ nm}$: 0.052, for methanol-extracted coloured materials), bearing the fatty acid profile of NL and FFA fractions, characterized by high percentages of saturated fatty acids (46.8% and 40.9% in NL and FFA, respectively) and monounsaturated fatty acids (45.9% and 35.1% in NL and FFA, respectively) and low percentages of polyunsaturated fatty acids (6.2% and 24.0% in NL and FFA, respectively) (Ramírez & Cava, 2004).

3.3. Evolution of colour parameters

3.3.1. General

Meat colour is chiefly determined by the chemistry of myoglobin, type of ligand bound to heme and state of the globin protein. Thus, upon heating, as in cooking, the globin protein will denature (Ledward, 1971), and the oxidation of purplish-red myoglobin (deoxymyoglobin), or bright red oxymyoglobin to brown metmyoglobin is accelerated. On heating, red meat therefore turns to a brown colour, due to the formation of ferric hemichromes. These changes are described when the core temperature is around 55–75 °C (Hunt, Sorheim, & Slide, 1999). During cooking of meat, oxymyoglobin denaturation and oxidation occurs and, at the same time, the metmyoglobin and other small molecule contents increase (Yongliang Liu & Yud-Ren Chen, 2001). Additionally in fried meat, Maillard reactions between reducing sugars and amino groups take place, contributing to the brown colour as a result of dehydration and temperature (Hodge, 1953).

In general, instrumental colour values of samples of loin chops fried in different culinary fats showed a slight decrease during refrigerated storage.

3.3.2. Evolution of lightness (L^*)

ANOVA results for lightness indicated significant differences due to the type of culinary frying fat used ($p = 0.000$) but not for the time of storage ($p = 0.340$) (Table 3). Fig. 2 shows changes in lightness (CIE L^*) of pork loin chops fried in different culinary fats during refrigerated storage. L^*-values showed a slight drop throughout time of storage, probably due to a loss of moisture.

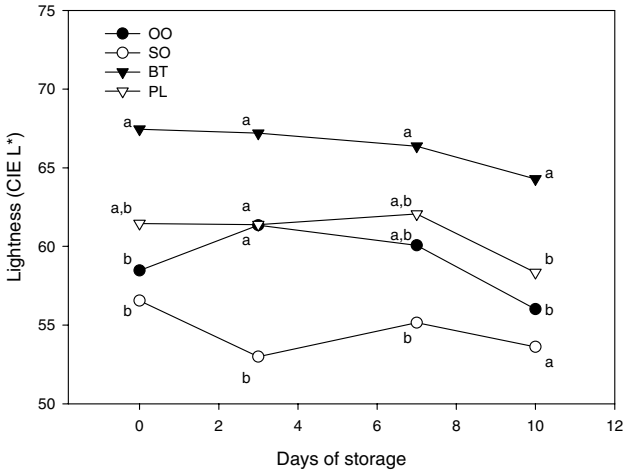

Fig. 2. Evolution of lightness (CIE L^*) in pork loin chops (*m. Longissimus dorsi*) fried in different culinary fats and stored at +4 °C (a,b: Different letters for the same day of refrigerated storage denote a statistical difference (Tukey test, $p < 0.05$); OO: olive oil; SO: sunflower oil; BT: butter; PL: pig lard).

The Tukey's test, applied to the type of culinary fat, showed significant differences at days 0, 3, 7 and 10 between groups. BT sample L^*-values were significantly higher ($p < 0.05$) than those from SO sample during all days of refrigerated storage. However, OO and PL simples exhibited intermediate L^*-values.

3.3.3. Evolution of redness (a^*)

ANOVA results for redness (CIE a^*) indicated significant differences due to the type of culinary frying fat used ($p = 0.000$) and time of storage ($p = 0.000$) (Table 3). Fig. 3 shows changes in redness (CIE a^*) of pork loin chops fried in different culinary fats during refrigerated storage. a^*-values of frying samples significantly dropped after 10 days of refrigerated storage. Changes in a^*-value during refrigeration could be attributable to the effect of lipid oxidation products on pigments responsible for the colour of fried meat.

Redness (a^*-value) is a parameter related to freshness in raw meat and associated with the chemical state of the myoglobin. In cooked meat, myoglobin is denatured or oxidized to metmyoglobin.

The Tukey's test, applied to the type of culinary fat, showed significant differences at day 3 between groups. BT samples showed the lowest a^*-values at days 0, 3, 7 and 10, being only significantly lower ($p < 0.05$) than OO, SO and PL at day 3.

3.3.4. Evolution of yellowness (b^*)

ANOVA results for yellowness indicated significant differences due to the type of culinary frying fat used

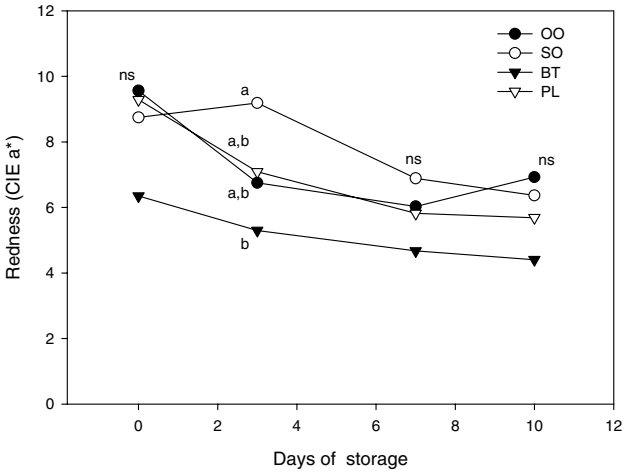

Fig. 3. Evolution of redness (CIE a^*) in pork loin chops (*m. Longissimus dorsi*) fried in different culinary fats and stored at +4 °C (a,b: Different letters for the same day of refrigerated storage denote a statistical difference (Tukey test, $p < 0.05$); OO: olive oil; SO: sunflower oil; BT: butter; PL: pig lard).

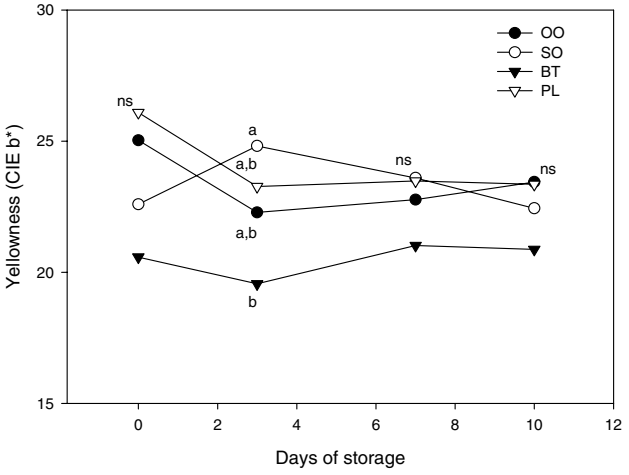

Fig. 4. Evolution of yellowness (CIE b^*) in pork loin chops (*m. Longissimus dorsi*) fried in different culinary fats and stored at +4 °C (a,b: Different letters for the same day of refrigerated storage denote a statistical difference (Tukey test, $p < 0.05$); OO: olive oil; SO: sunflower oil; BT: butter; PL: pig lard).

($p = 0.001$) but not for the time of storage ($p = 0.506$) (Table 3). Fig. 4 shows changes in yellowness (CIE b^*) of pork loin chops fried in different culinary fats during refrigerated storage. b^*-values remained unchanged in all groups during refrigerated storage, contrasting with the trend previously described for L^*-value and a^*-value. The Tukey's test, applied to the type of culinary fat, showed significant differences at day 3 between groups, values being significantly lower in BT ($p < 0.05$) than in the other groups.

3.3.5. Evolution of chroma (c^*)

ANOVA results for chroma indicated significant differences due to the type of culinary frying fat used

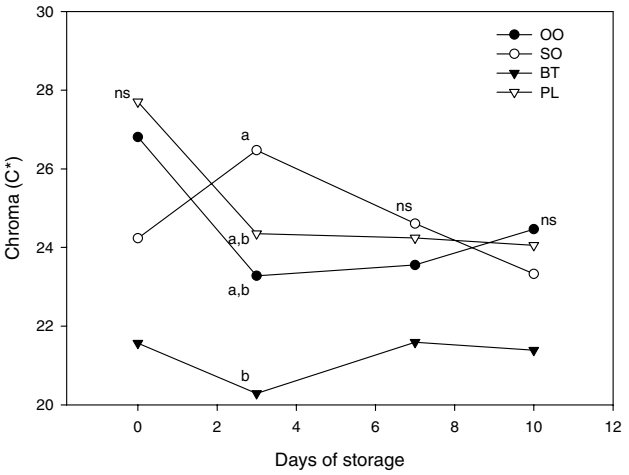

Fig. 5. Evolution of chroma (CIE c^*) in pork loin chops (*m. Longissimus dorsi*) fried in different culinary fats and stored at +4 °C (a,b: Different letters for the same day of refrigerated storage denote a statistical difference (Tukey test, $p < 0.05$); OO: olive oil; SO: sunflower oil; BT: butter; PL: pig lard).

($p = 0.001$) but not for the time of storage ($p = 0.206$) (Table 3). Fig. 5 shows changes in chroma (CIE c^*) of pork loin chops fried in different culinary fats during refrigerated storage. c^*-values did not change significantly during refrigerated storage. The Tukey's test, applied to the type of culinary fat, showed significant differences at day 3 between groups.

3.3.6. Evolution of hue ($h°$)

ANOVA results for hue (CIE $h°$) indicated significant differences due to the type of culinary frying fat used ($p = 0.000$) and time of storage ($p = 0.000$) (Table 3). Changes in hue (CIE $h°$) of pork loin chops fried in different culinary fats during refrigerated storage are shown in Fig. 6. Hue-value tended to increase with the time of refrigerated storage. Due to $h°$-value being calculated from the a^*-value and b^*-value, changes in one of these parameters will affect it. In this sense, the increase in $h°$-value being due to the decrease in a^*-value with storage time and the absence of noticeable changes in b^*-value. The Tukey's test, applied to the type of culinary fat, showed significant differences at day 3 between groups. BT samples showed the highest $h°$-value while SO samples had the lowest (BT = 74.82 vs SO = 69.86, $p < 0.05$).

All colour parameters showed a similar trend, showing statistical differences only at day 3 of refrigerated storage, there being no statistical differences between groups at the end of storage. This could be attributed to the fact that the differences between the colours of the samples fried in the different culinary fats disappeared as the time of storage increased, possibly oxidation of non-denatured myoglobin or changes in heat-induced pigments. However, more studies are

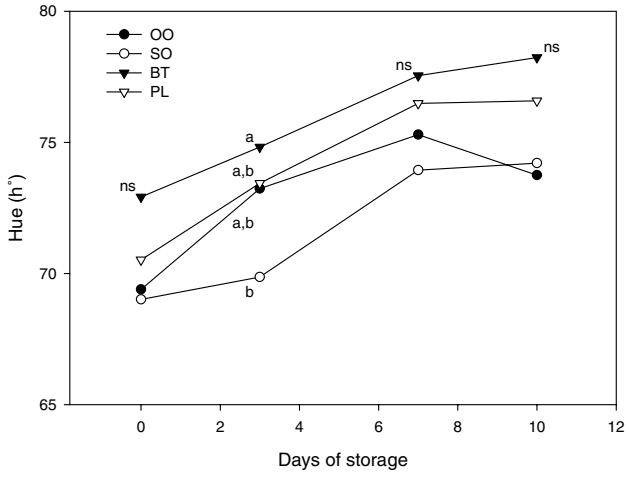

Fig. 6. Evolution of hue (CIE $h°$) in pork loin chops (*m. Longissimus dorsi*) fried in different culinary fats and stored at +4 °C (a,b: Different letters for the same day of refrigerated storage denote a statistical difference (Tukey test, $p < 0.05$); OO: olive oil; SO: sunflower oil; BT: butter; PL: pig lard).

necessary to reveal the exact factors involved in the colour changes of stored fried meat.

Roberts (1971) reported that myoglobin is one of the more heat-stable of the sarcoplasmic proteins and is almost completely denatured within a temperature range of 80–85 °C. As temperatures reached on the surface of loin chops were above the denaturation temperature of myoglobin, changes in the meat colour during storage could not be attributed to modifications of the chemical state of myoglobin but could be related to denatured myoglobin and/or coloured compounds formed from Maillard reactions. No relevant data have been found concerning the effect of culinary frying fat on colour changes in refrigerated stored meat, so it is not possible to compare and discuss the results.

3.4. Pearson's correlations between absorbances of extracted coloured materials with different solvents and lipid oxidation and colour

Pearson's correlations between TBARS, instrumental colour values and absorbances to coloured material extracted using different solvents (deionized water, methanol, ethanol and acetone) of pork loin chops fried in different culinary fats are shown in Table 4. At day 0, no significant ($p > 0.05$) correlations were found between TBARS values and absorbances, at 420 nm, of coloured compounds extracted with different solvents. The significant role played by Maillard reaction prod-

Table 4
Pearson's correlation coefficients between TBARS, colour instrumental values and absorbances of coloured material extracted using different solvents (deionized water, methanol, ethanol and acetone) of pork loin chops fried in different culinary fats at different days of refrigerated storage

		Solvents			
		Deionized water	Methanol	Ethanol	Acetone
Day 0	TBARS	0.059	0.298	0.010	−0.048
	L^*	−0.513*	−0.517*	−0.030	0.253
	a^*	0.368	0.667**	0.240	0.031
	b^*	0.306	0.667**	0.257	0.255
	c^*	0.322	0.678**	0.257	0.220
	$h°$	−0.337	−0.427	−0.143	0.247
Day 3	TBARS	−0.241	−0.273	0.292	0.306
	L^*	0.306	0.244	0.226	0.217
	a^*	−0.550*	−0.229	0.18	0.07
	b^*	0.012	0.331	0.462	0.782
	c^*	0.499*	0.222	−0.162	0.129
	$h°$	0.025	0.346	0.506	0.61
Day 7	TBARS	−0.062	−0.137	−0.003	0.117
	L^*	0.794	0.563	0.992	0.645
	a^*	−0.527*	−0.313	0.177	0.114
	b^*	0.017	0.179	0.469	0.652
	c^*	0.437	0.379	−0.086	0.242
	$h°$	0.054	0.100	0.728	0.334
Day 10	TBARS	−0.397	−0.783**	0.085	0.516
	L^*	0.142	0.001	0.773	0.071
	a^*	−0.587**	−0.505*	0.140	0.239
	b^*	0.006	0.023	0.567	0.340
	c^*	0.468*	0.538*	−0.265	0.085
	$h°$	0.037	0.014	0.273	0.739

* Significant Pearson's correlation at level $p < 0.05$.
** Significant Pearson's correlation at level $p < 0.01$.

ucts in colour formation found in fried loin chops was confirmed by the significant correlations found between absorbances, at 420 nm, of coloured extracted compounds and colour coordinates. In this sense, absorbances of coloured compounds extracted with methanol positively correlated with redness (a^*) (Pearson's correlation = +0.667, $p < 0.01$), yellowness (b^*) (Pearson's correlation = +0.667, $p < 0.01$) and colour saturation (c^*) (Pearson's correlation = +0.678, $p < 0.01$). However, lightness of fried samples negatively correlated with absorbances of coloured compounds extracted with deionized water (Pearson's correlation = −0.513, $p < 0.05$) and methanol (Pearson's correlation = −0.517, $p < 0.05$). Absorbances of ethanol- and acetone-extracted coloured material did not show any significant correlations ($p > 0.05$) with lipid oxidation on colour values, indicating a poor contribution to these traits. Data obtained are in agreement with the scientific literature. Numerous papers have reported the close correlations between browning and MRPs formed during cooking (reviewed by Manzocco, Calligaris, Mastrocola, Nicoli, & Lerici, 2001); however, no information is available concerning coloured materials extracted with different solvents and their colour coordinates.

At day 10, correlation analysis between TBARS values and absorbances at 420 nm of methanol-extracted coloured materials was negative ($R^2 = -0.783$, $p < 0.01$), indicating an important antioxidant effect of MRPs extracted with methanol. Numerous authors have found a positive correlation between colour and oxidative capacity of MRPs in model systems (Lim, Kim, & Moon, 1997; Tanaka, Sugita, Chiu, Nagashima, & Tagachi, 1990; Tubaro, Micossi, & Ursini, 1996). However, methanol-extracted coloured fraction was not the majority fraction and it may be possible that coloured material in this fraction could posses a higher antioxidant activity. Bailey and Um (1992) described the effectiveness of MRPs for prevention of lipid oxidation in refrigerated cooked meat, avoiding the development of WOF. The antioxidant activity of MRPs was attributed by Wagner, Derkits, Herr, Schuh, and Elmadfa (2002) to two possible mechanisms: (i) to the suppression of formation of peroxides acting as free radical scavengers and (ii) to the interaction with tocopherol of the oil or meat acting synergistically, regenerating the tocopherols. Regarding colour measurements at day 10, the a^*-value negatively correlated with the absorbances at 420 nm of water- ($R^2 = -0.587$, $p < 0.01$) and methanol- ($R^2 = -0.505$, $p < 0.05$) extracted coloured materials. On the other hand, the c^*-value positively correlated with the absorbances at 420 nm of water ($R^2 = +0.468$, $p < 0.05$) and methanol- ($R^2 = +0.438$, $p < 0.05$) extracted coloured materials. Thus, colour stability of the samples during refrigerated storage could be attributable in part to the antioxidant activity of these types of compounds.

4. Conclusions

The use of different culinary fats for frying of meat affects to the evolution of lipid oxidation and colour when fried meat is refrigerated. The use of oils with a greater oxidative stability, such as olive oil, increases the shelf-life of refrigerated fried meat, and avoids the development of undesirable changes, possibly due to the incorporation of antioxidant compounds and the modification of the fatty acid profile of meat. MRPs formation, measured as coloured extracted compounds, depends on the type of culinary fat used in frying and affects colour of the fried meat and increases the oxidative stability of meat during refrigerated storage. Even though, refrigerated fried meat tends toward discolouration, some evidence indicates that certain compounds formed during frying could favourably help to maintain a stable colour of the fried loin chops during storage.

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