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Fatty acid profiles of intramuscular fat from pork loin chops fried in different culinary fats following refrigerated storage

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Abstract

Changes in fatty acid profiles of pork loin chops fried in different culinary fats (olive oil, sunflower oil, butter and pig lard) during 10 days of refrigerated storage were studied. Olive oil-fried loin chops (OOLC) were significantly highest in monounsaturated fatty acids (MUFA) and C18:1. Sunflower oil-fried loin chops (SOLC) showed the highest polyunsaturated fatty acid (PUFA) proportions, mainly due to C18:2 contents. Butter-fried loin chops (BTLC) were significantly richer in saturated fatty acids (SFA), such as C12:0, C14:0 and C16:0, while pig lard-fried loin chops (PLLC) contained moderate proportions of SFA, MUFA and PUFA. Fatty acid profiles of neutral lipids (NL), free fatty acids (FFA) and polar lipids (PL) were slightly changed after refrigerated storage. After 10 days of refrigerated storage, differences among samples fried in different culinary fats were maintained or increased. NL from OOLC had the significantly largest percentages of C18:1 and MUFA, while SOLC had the significantly largest percentages of C18:2 and PUFA. The highest percentages of C12:0, C14:0, C16:0 and SFA were characteristic for pork loin chops fried in butter at the end of the storage period. Refrigerated pork loin chops fried in pig lard showed intermediate percentages of SFA, MUFA and PUFA. OOLC had a more desirable nutritional value than other fried pork loin chops after and before the refrigerated storage.

Keywords: Culinary fat; Meat; Refrigeration; Fatty acids; Deep-frying

1. Introduction

At present, frying is a culinary practice of great importance as a result of the increase in consumption of fried-foods due to the improvement of their palatability and quick preparation (Romero, Cuesta, & Sánchez-Muniz, 2001;Varela & Ruiz-Roso, 2000). These facts allow fried-foods to be consumed in large amounts, with an important role in dietary fat intake (Saguy & Pinthus, 1995).

Frying produces several modifications in meat, such as water losses (Singh, 1995) and changes in the fatty acid profiles of fat, which tend to be similar to culinary fat as a result of the exchange between fat from frying media and food (Sánchez-Muniz, Viejo, & Medina, 1992). Also, antioxidant substances are incorporated in meat by means of absorption from culinary fat. Vegetable oils, such as olive and sunflower oils, are very rich in these antioxidant substances, such as vitamin E and phenolic compounds (Quiles, Ramırez-Tortosa, Gómez, Huertas, & Mataix, 2002). During frying, high temperatures are reached on the food surface which promote the development of both undesirable and desirable reactions, such as lipid thermo-oxidation (Bastida & Sánchez-Muniz, 2001;Romero, Cuesta, & Sánchez-Muniz, 2000a), and the Maillard reactions (Whitfield, 1992). Several authors have suggested the formation of certain compounds with antioxidant activity as a result of development of Maillard reaction in fried foods, playing an important role in the control of lipid oxidation in fried

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meat and stored fried meat (Bailey, 1988;Ramırez, Morcuende, Estévez, & Cava, 2004).

The storage of cooked meat contributes to the deterioration of meat quality, mainly due to the development of lipid oxidation (Pearson, Love, & Shortland, 1977). Susceptibility of meat to lipid oxidation depends on several factors, such as (i) the unsaturated fatty acid content (Mistry & Min, 1992;Porter, Caldewell, & Mills, 1995); (ii) the fatty acid composition of lipid fractions (Morrissey, Sheehy, Galvin, Kerry, & Buckley, 1998;Nawar, 2000) and (iii) the balance between antioxidant/prooxidant factors (Cava, Ventanas, Tejeda, Ruiz, & Antequera, 2000;Gray, Gomaa, & Buckley, 1996). Meat cooking causes the disorganization of cell structures, leading to polyunsaturated fatty acid and prooxidant interactions favouring the development of lipid oxidation (Reineccius, 1979;Rhee, 1988). Lipid oxidation, is one of the most important degradation processes during meat refrigeration (Alasnier & Gandemer, 1998), however, this phenomena plays a less important role in cooked meat, due to the fact heating induces the thermal denaturation of lipolytic muscle enzymes, and this inactivation is believed to contribute to reduction of the release of free fatty acids (Estévez, Ventanas, & Cava, 2004).

Lipid oxidation-derived products cause alteration of quality attributes of meat. Lipid oxidation leads to rancidity in meat, which is associated with the development of warmed-over-flavour in refrigerated cooked meat (Byrne et al., 2001;Poste, Willemont, Butler, & Patterson, 1986;St. Angelo, Crippen, Dupuy, & James,. 1990). Besides changes in sensory quality, lipid oxidation causes a reduction of the nutritive value of meat as a result of oxidation of essential fatty acids (Donelli & Robinson, 1995; Romero, Sánchez-Muniz, & Cuesta, 2000b; Sánchez-Muniz et al., 1994) and vitamins (Fillion & Henry, 1998)

The aim of the study was to evaluate the effect of the type of culinary frying fat on the changes of fatty acid of lipid fractions extracted from fried pork loin chops after refrigerated storage.

2. Material and methods

2.1. Materials

Olive oil (OL) (acidity 0.4% as oleic acid and with a content of alpha-tocopherol of 20 mg/100 g), refined sunflower oil (SO) (acidity 0.2% as oleic acid and with a content of alpha-tocopherol of 60 mg/100 g), butter (BT) and pig lard (PLD) were used as culinary frying fats. The choice of such culinary fats was based both on the fact that these fats are used in different gastronomy cultures and their fat composition (OL being high in monounsaturated fatty acids, SO being high in polyunsaturated fatty acids, BT being high in saturated fatty acids, and PLD being high in saturated and monounsaturated fatty acids) (Table 1). Pork loin (m. *Longissimus dorsi*) from Large-White x Duroc pigs was sliced using a slicing machine, giving 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 OL, SO, BT or PLD. Frying was performed on an electric stove at 160 °C in domestic stain-

Table 1
Fatty acid (FA) profiles of culinary fats before and after frying (% of total FA)

Oils	OO		SO		BT		PLD	
	Before	After	Before	After	Before	After	Before	After
C12:0	0.0	0.0	0.0	0.0	3.7	3.3	0.0	0.1
C14:0	0.0	0.0	0.1	0.1	13.4	12.1	1.2	1.2
C16:0	10.1	9.9	6.3	6.3	39.5	34.6	23.0	23.5
C17:0	0.0	0.2	0.0	0.0	0.7	0.6	0.5	0.5
C18:0	3.3	3.4	3.8	4.0	11.0	13.3	12.6	12.9
C20:0	0.4	0.5	0.3	0.3	0.1	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	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	4.0	2.7	16.2	15.9

OO, olive oil; SO, sunflower oil; BT, butter; PLD, pig lard.
SFA, saturated fatty acids (C12:0, C14:0, C16:0, C17:0, C18:0, C20:0); MUFA, monounsaturated fatty acids (C16:1, C17:1, C18:1, C20:1); PUFA, polyunsaturated fatty acids (C18:2, C18:3, C20:2, C20:4).

less steel-teflon fryers of 2 l-capacity. Culinary fats were used once with the food/oil ratio being 20 g/500 ml. The frying lasted 2 min, and samples were turned round after 1 min of 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. After frying, samples were placed on Styrofoam meat trays and over-wrapped in PVC oxygen-permeable films and stored at +4 °C for 10 days under fluorescent light. Cooked samples were stored at −80 °C prior to analysis.

2.3. Lipid isolation, fractionation and fatty acid profile determination

Lipids were extracted from 2 g of sample with chloroform/methanol (1:2), according to the method described by Bligh and Dyer (1959). Total lipid extracts were fractionated into neutral lipids (NL), free fatty acids (FFA) and polar lipids (PL) by solid phase extraction on 100 mg aminopropyl minicolumns (Varian, CA), following the procedure described by Monin, Hortós, Diaz, Rock, and Garcia-Regueiro (2003). Fatty acid methyl esters (FAME) and dimethylacetals (DMA) from fatty acids and fatty aldehydes 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). FAME and DMA were analyzed using a Hewlett–Packard, model HP-5890A, gas chromatograph, equipped with a flame ionisation detector (FID). The derivatives were separated on a semi-capillary column (Hewlett–Packard FFAP-TPA fused-silica column, 30m 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. Identifications of FAMEs and DMAs were based on retention times of reference compounds (Sigma–Aldrich) and mass spectrometry. Fatty acid and fatty aldehyde composition was expressed as percent of total fatty acid methyl esters and total dimethyl acetals.

2.4. Data analysis

In order to determine the effect of the type of culinary fat on of fatty acid composition of lipid fractions on each day of study (day 0 and day 10), a one-way analysis of variance (ANOVA) was used. HSD Tukey's tests were used when ANOVA found significant differences between treatments. The effect of time of storage on changes in fatty acid composition for each type of culinary fat was determined using a Student's *t*-test ($p < 0.05$). Principal component analysis (PCA) was performed to determine relationships between variables and samples. Statistical analyses were performed using a SPSS 11.5 software package (SPSS, 1999).

3. Results and discussion

3.1. Fatty acid profiles of intramuscular lipid fractions of pork loin chops fried in different culinary fats

Fatty acid profiles of the different culinary frying fats before and after frying are shown in Table 1. Fatty acid profiles of culinary fats did not change after frying and this fact could be attributable to the small time of frying (frying at 160 °C for 2 min), the large culinary oil volume/meat ratio (2000 ml culinary fat/80 g meat) and the small number of uses of culinary fats (5 fryings/each culinary fat) (Melton, Jafar, Sykes, & Trigiano, 1994).

Tables 2–4 show the fatty acid composition of neutral lipids, free fatty acids and polar lipids, respectively, of intramuscular lipids from fried pork loin chops in different culinary fats after frying and refrigerated storage.

Table 2 indicates that the relative proportions of saturated (SFA), monounsaturated (MUFA) and polyunsaturated fatty acids (PUFA) of NL from pork loin chops were significantly different in pork loin chops fried in the different culinary fats. Olive oil-fried loin chops (OOLC) were significantly higher in MUFA and oleic acid (C18:1 $n-9$), while sunflower oil-fried loin chops (SOLC) showed the highest PUFA, mainly due to linoleic acid (C18:2 $n-9$). On the other hand, butter-fried loin chops (BTLC) were significantly richer in SFA, such as lauric (C12:0), miristic (C14:0) and palmitic (C16:0) acids, while pig lard-fried loin chops (PLLC) contained moderate proportions of SFA, MUFA and PUFA. These results indicate that the fatty acid composition of NL of the fried loin chops tends to be similar to the culinary frying fat, agreeing with findings previously reported by Candela, Astiasaran, and Bello (1996) and Sánchez-Muniz et al. (1992) in poultry, pork and sardines fried in olive and sunflower oils and pig lard.

FFA profiles were found to significantly differ among loin chops fried in different culinary fats (Table 3). In the same way as NL fractions, FFA of fried loin chops reflected the fatty acid profile of the culinary fats in which they were fried. Thus, C12:0 and SFA percentages were significantly ($p < 0.05$) higher in BTLC, whereas significantly ($p < 0.05$) lower percentages of C18:1 and MUFA were found in SOLC, PLLC and BTLC than in OOLC. SOLC showed the highest proportion ($p < 0.05$) of C18:2 compared to the other fried samples. These results could be related to the fact that heat and moisture are both important factors influencing hydrolysis of ester bonds in heated oils, resulting in the liberation of free fatty acids, mono- and diacylglycerides (White, 1991) which alter FFA profiles. The high susceptibility to lipid oxidation of FFA (Nawar, 1984), and especially polyenoic fatty acids, could make SOLC more sensitive to lipid oxidation, leading to more development of rancidity

Table 2
Effect of type of culinary fat and refrigerated storage time (0 and 10 days) on fatty acid composition of neutral lipids from intramuscular fat of pork loin chops (% of total FA)

	Day 0						Day 10					
	OOLC	SOLC	BTLC	PLLC	SEM	*p*	OOLC	SOLC	BTLC	PLLC	SEM	*p*
C12:0	0.1^{b}	0.1^{b}	1.1^{a}	$0.3^{b\ x}$	0.10	0.000	0.1^{b}	0.0^{b}	0.9^{a}	$0.1^{b\ y}$	0.09	0.000
C14:0	0.8^{b}	0.8^{b}	4.7^{a}	1.5^{b}	0.38	0.000	0.7^{b}	0.6^{b}	4.3^{a}	1.5^{b}	0.36	0.000
C16:0	$19.3^{c\ x}$	17.0^{c}	28.9^{a}	25.3^{b}	1.13	0.000	$17.9^{c\ y}$	15.2^{d}	29.1^{a}	25.6^{b}	1.32	0.000
C17:0	0.2^{b}	0.2^{b}	0.4^{ab}	0.5^{a}	0.04	0.000	0.2	0.1	0.3	0.3	0.03	0.094
C18:0	8.6^{b}	$8.9^{b\ x}$	$12.6^{a\ x}$	11.8^{a}	0.45	0.000	7.4^{b}	$7.5^{b\ y}$	$13.6^{a\ y}$	12.3^{a}	0.66	0.000
C20:0	0.3^{a}	0.2^{ab}	0.2^{b}	0.3^{ab}	0.02	0.040	0.3^{a}	0.3^{ab}	0.2^{b}	0.3^{ab}	0.01	0.038
SFA	$29.2^{c\ x}$	27.1^{c}	46.8^{a}	$39.4^{b\ x}$	1.90	0.000	$26.4^{c\ y}$	23.8^{c}	47.5^{a}	$40.1^{b\ y}$	2.29	0.000
C16:1	2.5^{b}	2.0^{c}	3.6^{a}	3.5^{a}	0.16	0.000	2.3^{b}	1.8^{b}	3.3^{a}	3.7^{a}	0.19	0.000
C17:1	0.2^{b}	0.1^{b}	0.2^{a}	0.3^{b}	0.02	0.000	0.2^{b}	0.1^{c}	0.2^{a}	0.2^{a}	0.01	0.000
C18:1	59.1^{a}	37.5^{c}	41.2^{b}	43.8^{b}	1.92	0.000	62.3^{a}	36.2^{c}	40.9^{b}	44.5^{b}	2.30	0.000
C20:1	0.8^{b}	0.7^{b}	0.8^{b}	1.1^{a}	0.04	0.000	0.8^{ab}	0.6^{b}	0.8^{ab}	1.1^{a}	0.06	0.028
MUFA	62.5^{a}	40.4^{c}	45.9^{b}	48.6^{b}	1.90	0.000	65.6^{a}	38.8^{d}	45.2^{c}	49.5^{b}	2.32	0.000
C18:2	$6.9^{b\ x}$	31.3^{a}	5.0^{b}	10.2^{b}	2.49	0.000	$6.8^{b\ y}$	36.6^{a}	5.8^{b}	8.8^{b}	3.03	0.000
C18:3	0.5^{b}	0.3^{c}	$0.4^{c\ x}$	$0.6^{a\ x}$	0.03	0.000	0.5^{a}	0.2^{b}	$0.3^{ab\ y}$	$0.7^{a\ y}$	0.05	0.004
C20:2	0.1^{b}	$0.2^{b\ x}$	0.2^{b}	0.5^{a}	0.04	0.000	0.2^{b}	$0.2^{b\ y}$	0.2^{b}	0.4^{a}	0.03	0.000
C20:4	0.7	0.7	0.6	0.5	0.05	0.535	0.5	0.4	0.3	0.4	0.03	0.315
PUFA	$8.2^{bc\ x}$	32.5^{a}	6.2^{c}	11.8^{b}	2.48	0.000	$7.9^{b\ y}$	37.4^{a}	6.6^{b}	10.3^{b}	3.00	0.000
$n-3$	0.5^{b}	0.3^{c}	$0.4^{c\ x}$	$0.6^{a\ x}$	0.03	0.000	0.5^{a}	0.2^{b}	$0.3^{ab\ y}$	$0.7^{a\ x}$	0.05	0.004
$n-6$	$7.8^{b\ x}$	32.2^{a}	5.8^{b}	11.2^{b}	2.49	0.000	$7.4^{b\ y}$	37.2^{a}	6.3^{b}	9.7^{b}	3.03	0.000
$n-6/n-3$	15.6^{b}	$107.3^{a\ x}$	$14.5^{b\ x}$	$18.7^{b\ x}$	11.31	0.000	14.8^{c}	$186.2^{a\ y}$	$21.0^{b\ y}$	$13.9^{c\ y}$	64.70	0.144
NV	3.3^{a}	3.9^{a}	1.3^{b}	$2.0^{b\ x}$	0.26	0.000	3.7^{a}	4.7^{a}	1.4^{b}	$2.0^{b\ y}$	0.33	0.000

OOLC, olive oil-fried loin chops; SOLC, sunflower oil-fried loin chops; BTLC, butter-fried loin chops; PLLC: pig lard-fried loin chops.
p, probabilities of the one-way ANOVA.
SFA, saturated fatty acids (C12:0, C14:0, C16:0, C17:0, C18:0, C20:0); MUFA, monounsaturated fatty acids (C16:1, C17:1, C18:1, C20:1); PUFA, polyunsaturated fatty acids (C18:2, C18:3, C20:2, C20:4); $n-3$: omega-3 fatty acids (C18:3); $n-6$: omega-6 fatty acids (C18:2, C20:2; C20:4). NV, nutritive value (C18:1 + C18:2)/(C12:0 + C14:0 + C16:0).
a, b, c: means with different superscripts for the same day of storage are statistically different (Tukey's test, $p < 0.05$).
x, y: means with different letter for the same culinary fat are statistically different (Student's *t* test, $p < 0.05$).

during storage than in samples fried in the other culinary fats.

The fatty acid composition of PL slightly differed among samples fried in different culinary fats (Table 4), and only C18:0 showed a statistical difference among loins chops fried in the different culinary fats on day 0. In this sense, PL from PLLC showed a lower percentage of C18:0 than did OOLC. PUFA in the phospholipids are important sources of lipid-derived flavour compounds during cooking (Mottram & Edwards, 1983;Mottram, 1998). PL are considered to be prime targets for lipid oxidation because, in addition to their high degree of unsaturation, they are exposed to proteins and other catalysts of lipid oxidation as components of membranes in contact with the cytosol (Boylston et al., 1996). Because of the low oxidative stability of these fatty acids, it seems likely that changes in their concentration, even small, would result in alterations of the composition of the aroma volatiles produced during frying. Differences in fatty acid profiles, particularly NL and FFA fractions, are due to oil uptake of meat during the frying process (Ramırez & Cava, 2004;Sánchez-Muniz et al., 1992). These findings indicate that the modifications in fatty acid composition of fried samples are due to the exchange between the NL and FFA which constitute frying oils and NL and FFA fractions of meat, while PL remain unchanged after frying due to fact that this lipid fraction makes up membrane cell structure in which fatty acids are not easily exchanged.

3.2. Changes in fatty acid profiles of intramuscular lipid fractions of pork loin chops fried in different culinary fats after refrigerated storage

No large modifications in fatty acid profiles of NL, FFA and PL fractions were found after refrigerated storage and the changes depended on the type of culinary frying fat (Tables 2–4). In NL, SFA tended to decrease in OOLC ($p < 0.05$) and SOLC ($p > 0.05$) and tended to increase in BTLC ($p > 0.05$) and PLLC ($p < 0.05$), as long as PUFA significantly ($p < 0.05$) decreased in OOLC. In the FFA fraction, C16:0 percentages tended to increase, but not to a significant extent ($p > 0.05$) in OOLC and SOLC, similarly to the decrease observed in the NL fraction, while C18:0 percentages significantly increased ($p < 0.05$) in SOLC after refrigerated storage. Although not to a significant extent,

Table 3
Effect of type of culinary fat and refrigerated storage time (0 and 10 days) on fatty acid composition of free fatty acids from intramuscular fat of pork loin chops (% of total FA)

	Day 0						Day 10					
	OOLC	SOLC	BTLC	PLLC	SEM	*p*	OOLC	SOLC	BTLC	PLLC	SEM	*p*
C14:0	1.2^{b}	0.9^{b}	2.5^{a}	1.3^{b}	0.15	0.000	0.9^{c}	1.0^{bc}	2.4^{a}	1.4^{b}	0.15	0.000
C16:0	16.2	17.9	22.6	20.1	1.00	0.116	17.7^{b}	18.4^{b}	21.2^{a}	18.4^{b}	0.43	0.008
C17:0	1.6^{x}	0.4^{x}	0.6	0.6^{x}	0.25	0.347	0.6^{y}	0.9^{y}	1.9	1.4^{y}	0.28	0.397
C18:0	13.0	11.1^{x}	13.1	12.6	0.38	0.202	10.9	14.0^{y}	13.9	13.1	0.47	0.057
C20:0	0.9	1.9^{x}	2.1^{x}	2.3^{x}	0.33	0.535	0.7	0.6^{y}	0.6^{y}	0.5^{y}	0.08	0.938
SFA	33.0^{a}	32.2^{a}	40.9^{a}	36.9^{ab}	1.16	0.014	30.8^{b}	34.8^{ab}	40.0^{a}	34.8^{ab}	0.97	0.002
C16:1	1.9	1.8^{x}	2.5	2.8	0.19	0.140	1.8	1.5^{y}	2.3	2.1	0.16	0.273
C17:1	0.2	0.1	0.1	0.2	0.03	0.576	0.1	0.0	0.2	0.1	0.04	0.503
C18:1	39.5^{a}	30.2^{b}	31.0^{b}	32.1^{b}	1.19	0.009	43.1^{a}	26.9^{b}	31.9^{b}	28.1^{b}	1.78	0.000
C20:1	0.7^{x}	2.1^{x}	1.4^{x}	2.0^{x}	0.26	0.220	0.5$^{ab\ y}$	0.4$^{b\ y}$	0.8$^{a\ y}$	0.5$^{ab\ y}$	0.06	0.031
MUFA	42.2^{a}	34.1^{b}	35.1^{b}	37.1^{ab}	1.05	0.015	45.5^{a}	28.8^{b}	35.2^{b}	30.9^{b}	1.79	0.000
C18:2	17.2^{b}	25.3^{a}	15.2^{b}	17.6^{b}	1.00	0.000	14.6^{bc}	24.5^{a}	14.3^{c}	19.8^{ab}	1.14	0.000
C18:3	1.3^{x}	1.9	2.3	2.2^{x}	0.16	0.139	4.5^{y}	6.0	5.1	8.8^{y}	0.66	0.089
C20:2	0.7	1.5	1.3	0.9	0.23	0.696	0.9	0.8	1.9	1.4	0.25	0.417
C20:4	5.5	5.1	5.4	5.3	0.24	0.945	3.7^{ab}	5.1^{a}	3.4^{b}	4.3^{ab}	0.24	0.048
PUFA	24.8^{b}	33.7^{a}	24.0^{b}	26.0^{b}	1.11	0.001	23.7^{b}	36.4^{a}	24.7^{b}	34.4^{a}	1.53	0.000
$n-3$	1.3^{x}	1.9	2.3	2.2^{x}	0.16	0.139	4.5^{y}	6.0	5.1	8.8^{y}	0.66	0.089
$n-6$	23.5^{b}	31.8^{a}	21.8^{b}	23.8^{b}	1.09	0.000	19.2^{b}	30.4^{a}	19.6^{b}	25.6^{ab}	1.31	0.001
$n-6/n-3$	19.5^{x}	20.5	10.6	11.2	1.79	0.076	4.5^{y}	6.3	9.0	3.4	1.52	0.611

OOLC, olive oil-fried loin chops; SOLC, sunflower oil-fried loin chops; BTLC, butter-fried loin chops; PLLC, pig lard-fried loin chops.
p, probabilities of the one-way ANOVA.
SFA, Saturated fatty acids (C14:0, C16:0, C17:0, C18:0, C20:0); MUFA, monounsaturated fatty acids (C16:1, C17:1, C18:1, C20:1); PUFA, polyunsaturated fatty acids (C18:2, C18:3, C20:2, C20:4); $n-3$: omega-3 fatty acids (C18:3); $n-6$: omega-6 fatty acids (C18:2, C20:2; C20:4).
a, b, c: means with different superscripts for the same day of storage are statistically different (Tukey's test, $p < 0.05$).
x, y: means with different letter for the same culinary fat are statistically different (Student's *t* test, $p < 0.05$)

MUFA tended to increase ($p > 0.05$) in OOLC and tended to decrease in SOLC and PLLC ($p > 0.05$) whereas PUFA tended to increase ($p > 0.05$) in these last two. In PL, C18:2 proportions tended to decrease ($p > 0.05$) in all culinary fried chops after refrigerated storage. Findings are in contrast with the large changes in fatty acid profiles of lipid fractions reported by other authors in refrigerated cooked meat (Estévez et al., 2004). In this sense, even though heating induces thermo-oxidation of unsaturated fatty acids, heating produces the thermal denaturation of muscle lipolytic enzymes, leading to their partial or total inactivation, that could affect the release of FFA and therefore modifications of the fatty acid profiles of NL and PL (Estévez et al., 2004). Therefore, changes in fatty acid profiles of fried samples after refrigerated storage suggest that lipid oxidation could be the main process implicated in the changes of fatty acid profiles of stored samples, agreeing with results described previously by other authors (Estévez et al., 2004;Pearson et al., 1977). Findings are in agreement with Bognar (1998), Fillion and Henry (1998) and Ruiz-Roso (1998) who reported that frying is less injurious than other culinary treatments and heating technologies on vitamins and fatty acids, probably due to the intrinsic characteristics of the treatment and the role of heat-induced antioxidants formed, such as MRP, which could inhibit the development of oxidative processes. Although changes reported for fatty acid profiles from different lipid fractions did not show statistical differences in ANOVA, results suggest a different susceptibility to oxidative deterioration of loin chops fried in different culinary fats during refrigerated storage, especially in the more unsaturated ones (SOLC and OOLC). These differences could be attributable to different fatty acid compositions of lipid fractions and the amounts of natural antioxidants and MRP because of frying in different culinary fats, both affecting oxidative status of samples during refrigerated storage. In fact, Ramírez et al. (2004) reported an increase in lipid oxidation in loin chops fried in different culinary fats and the TBARS values were significantly lower in OOLC and SOLC than in PLLC and BTLC after refrigerated storage. Additionally, these authors found a negative correlation between TBARS and MRP extracted with different solvents from fried samples; and the contents of MRP extracted with methanol were significantly higher in OOLC and SOLC. The relative stability of the fatty acid profiles in all fried pork loin chops, especially in SOLC and OOLC, could be explained by the antioxidant activity of these compounds (Bailey, 1988;Manzocco et al., 2001) and the possible increase in tocopherol contents in SOLC an OOLC due to uptake of alpha-tocopherol from sunflower and olive oils (SO, 60 mg/100 g and OO, 20 mg/100 g).

Table 4
Effect of type of culinary fat and refrigerated storage time (0 and 10 days) on fatty acid and fatty aldehyde (AL) compositions of polar lipids from intramuscular fat of pork loin chops (% of total FA)

Fatty acids	Day 0						Day 10					
	OOLC	SOLC	BTLC	PLLC	SEM	*p*	OOLC	SOLC	BTLC	PLLC	SEM	*p*
C14:0	0.1	0.1	0.2	0.1	0.01	0.051	0.1	0.2	0.2	0.1	0.01	0.160
C16:0	11.0	9.5^{x}	11.9	12.2	0.40	0.063	9.2^{b}	$9.7^{ab\ y}$	11.8^{a}	11.5^{a}	0.36	0.007
C17:0	0.2	0.4^{x}	0.2	0.3^{x}	0.02	0.237	0.3	0.3^{y}	0.3	1.4^{y}	0.18	0.047
C18:0	19.7^{a}	19.0^{ab}	$18.1^{ab\ x}$	17.5^{b}	0.30	0.036	20.1	19.8	18.5^{y}	18.1	0.40	0.255
C20:0	0.0	0.0^{x}	0.0^{x}	0.0^{x}	0.01	0.169	0.2	0.0^{y}	0.6^{y}	0.7^{y}	0.15	0.370
SFA	30.9	28.8	30.3	29.8	0.28	0.053	29.6	29.6	31.1	30.4	0.38	0.474
C16:1	0.6^{x}	0.5	0.6	0.6	0.02	0.068	0.7^{y}	0.8	0.6	0.6	0.10	0.875
C17:1	0.2	0.3^{x}	0.2	0.3	0.02	0.237	0.3	0.3^{y}	0.3	0.4	0.04	0.448
C18:1	14.1	14.9	15.7	15.2	0.38	0.515	12.7^{b}	13.8^{ab}	16.4^{a}	14.8^{ab}	0.43	0.007
C20:1	0.3	0.6^{x}	0.4	0.3	0.04	0.096	0.5	0.5^{y}	0.4	0.4	0.02	0.390
MUFA	15.1	16.3	17.0	16.4	0.40	0.462	14.2^{b}	15.4^{ab}	17.7^{a}	16.2^{ab}	0.41	0.012
C18:2	29.7	29.2	29.7	30.7	0.28	0.323	27.6	26.7	28.1	28.3	0.37	0.431
C18:3	0.9	1.4	0.8^{x}	0.7	0.11	0.133	3.1	3.2	2.8^{y}	2.3	0.14	0.057
C20:2	1.1^{x}	1.3	0.9	1.2	0.07	0.143	$1.3^{ab\ y}$	1.6^{a}	1.1^{b}	0.9^{b}	0.08	0.003
C20:4	22.0	22.8	21.1	20.9	0.35	0.203	23.9^{a}	23.1^{ab}	18.9^{b}	20.5^{ab}	0.68	0.017
PUFA	53.7^{x}	54.7	52.5	53.5	0.40	0.288	$56.0^{a\ y}$	54.6^{ab}	51.0^{b}	52.0^{ab}	0.65	0.011
$n-3$	0.9	1.4	0.8^{x}	0.7	0.11	0.133	3.1	3.2	2.8^{y}	2.3	0.14	0.057
$n-6$	52.9	53.3	51.7	52.8	0.34	0.401	52.8^{a}	51.4^{ab}	48.1^{b}	49.7^{ab}	0.62	0.026
$n-6/n-3$	63.2	50.1^{x}	63.3	86.7^{y}	5.78	0.153	16.8	16.4^{x}	17.2	23.5^{y}	1.20	0.112
C16-AL	38.0	38.1	40.1	40.0	0.54	0.360	36.9	36.3	39.1	37.3	0.48	0.171
C18-AL	45.6	46.2^{x}	44.4	43.7	0.59	0.448	50.1	51.6^{y}	49.5	48.9	0.42	0.129
C18:1-AL	16.3	15.7	15.5	16.3	0.23	0.461	13.0	12.1	11.3	13.8	0.44	0.247
FA/DMA	15.5	17.7	18.0	17.7	0.56	0.376	19.4^{a}	18.2^{ab}	16.7^{ab}	15.8^{b}	0.52	0.047

OOLC, olive oil-fried loin chops; SOLC, sunflower oil-fried loin chops; BTLC, butter-fried loin chops; PLLC, pig lard-fried loin chops.
p, probabilities of the one-way ANOVA.
SFA, saturated fatty acids (C14:0, C16:0, C17:0, C18:0, C20:0); MUFA, monounsaturated fatty acids (C16:1, C17:1, C18:1, C20:1); PUFA, polyunsaturated fatty acids (C18:2, C18:3, C20:2, C20:4); $n-3$: omega-3 fatty acids (C18:3); $n-6$: omega-6 fatty acids (C18:2, C20:2; C20:4); FA/DMA, fatty acids/dimethyl acetals ratio.
a, b, c: means with different superscripts for the same day of storage are statistically different (Tukey's test, $p < 0.05$).
x, y: means with different letter for the same culinary fat are statistically different (Student's *t* test, $p < 0.05$).

3.3. Fatty acid profiles of intramuscular lipid fractions of pork loin chops fried in different culinary fats after 10 days of refrigerated storage

Differences described for pork loin chops fried in different culinary fats at day 0 were maintained or increased after refrigerated storage. In this sense, NL from OOLC had the significantly largest percentages of C18:1 and MUFA, while SOLC had the significantly largest percentages of C18:2 and PUFA. The highest percentages of C12:0, C14:0, C16:0 and SFA were characteristic of the fatty acid profile of pork loin chops fried in butter. Refrigerated pork loin chops fried in pig lard showed a fatty acid profile with more intermediate percentages of SFA, MUFA and PUFA than the other culinary fat-fried loins. Regarding FFA profiles, OOLC showed the highest percentages of C18:1 and MUFA and SOLC the highest percentages of C18:2 and PUFA, FFA from BTLC being the richest in C14:0, C16:0 and SFA. In relation to PL, BTLC showed higher proportions of C16:0, C18:1 and MUFA and a lower proportion of PUFA than OOLC, as a result of possible changes took place during refrigerated storage. PUFA, in contrast to MUFA, are very prone to oxidative degradation, leading to the generation of compounds related to rancidity and undesirable sensory perceptions of cooked and stored meat (Mottram, 1998), so volatile compounds and sensory properties of fried and stored loin chops might be different, depending on the type of culinary fat used.

3.4. Implications of the type of culinary fat and storage on nutritive aspects of fried loin chops

Frying with culinary fats and storage had important implications for nutritive value of fried loin chops, due to the alteration in fatty acid profiles (Table 2). Nutritionists have focussed on the type of PUFA and the balance in the diet between $n-3$ PUFA formed from C18:3 and $n-6$ PUFA formed from C18:2, recommending a ratio of less than 4. Regarding NL, which constitute the majority fraction of meat – approximately more than 80% of total lipids in intramuscular fat – the ratios of $n-6$:$n-3$ in OOLC (15.6), BTLC (14.5) and PLLC (18.7) loin chops were more close to

health recommendations than in SOLC (107) at day 0. After refrigerated storage, a reduction in the $n-6{:}n-3$ ratio was observed in OOLC (14.8) and PLLC (13.9, $p < 0.05$), while the ratio increased in BTLC (21.0, $p < 0.05$), being dramatically increased in SOLC (186, $p < 0.05$). The ratio of $n-6{:}n-3$ PUFA is also a risk factor for cancers and coronary heart disease, and especially for the formation of blood clots leading to a heart attack (Enser, 2001). Recently, Moreiras, Carvajal, and Cabrera (1998) have reported that the PUFA + MUFA/SFA ratio is used to indicate the fat quality of a food. Foods with a high PUFA + MUFA/SFA ratio have a more adequate fatty acid profile for protection against cardiovascular and other degenerative diseases. In OOLC (3.3, $p < 0.05$) and SOLC (3.9, $p < 0.05$) the calculated nutritional values (C18:1 $n-9$ + C18:2 $n-6$/C12:0 + C14:0 + C16:0) were significantly higher than in BTLC (1.3, $p < 0.05$) and PLLC (2.0, $p < 0.05$) after frying, and the initial differences in this ratio were much more larger among different fried loin chops after refrigerated storage (3.7, 4.7, 1.4 and 2.0, for OOLC, SOLC, BTLC and PLLC, respectively). Taking into consideration the fatty acid composition and nutritional recommendations and reported findings, both day 0 and day 10, OOLC gave a more '*desirable*' fatty acid profile and nutritional ratios – even when in some cases these ratios are far from desirable values – than did chops fried in the others kinds of culinary fats. On the contrary, BTLC had an unbalanced fatty acid profile and nutritional ratios very much far for nutritionist recommendations, particularly in the high content of SFA.

3.5. Multivariate analysis of fatty acids from intramuscular lipid fractions

A principal component analysis (PCA) was carried out to determine the relationship between the selected studied traits. PCA is a mathematical procedure for resolving sets of data into orthogonal components whose linear combinations (principal components) approximate the original data to any desired degree of accuracy. In most cases, two principal components are sufficient to explain a great proportion of the variation in the original variables, thus resulting in a considerable compression of the data. PCA of these variables resulted in four significant factors that accounted for 74.1% of the variability, 40.75% and 15.97% of the variability being explained by principal components (PC) #1 and #2, respectively. Fig. 1 shows the score plot of the different variables (coefficients of the eigenvectors) for the two first principal components (PC#1 and PC#2). In this plot, it is possible to distinguish a group of variables composed of C12:0, C14:0, C16:0 and C18:0 from NL and FFA fractions in the positive axis on the PC#1, far from the origin and explaining an important part of the variation. C18:2, components from NL and FFA fractions, are located on PC#2, far from the origin, explaining an independent cause of variation, and being opposite to the C18:1 from NL and FFA fractions. The distribution of the data on the two first PC (Fig. 2) shows four great separate groups of points, corresponding to the four different culinary frying fats and in which separation between fried and stored samples was not obtained. OOLC and SOLC are confined left along the

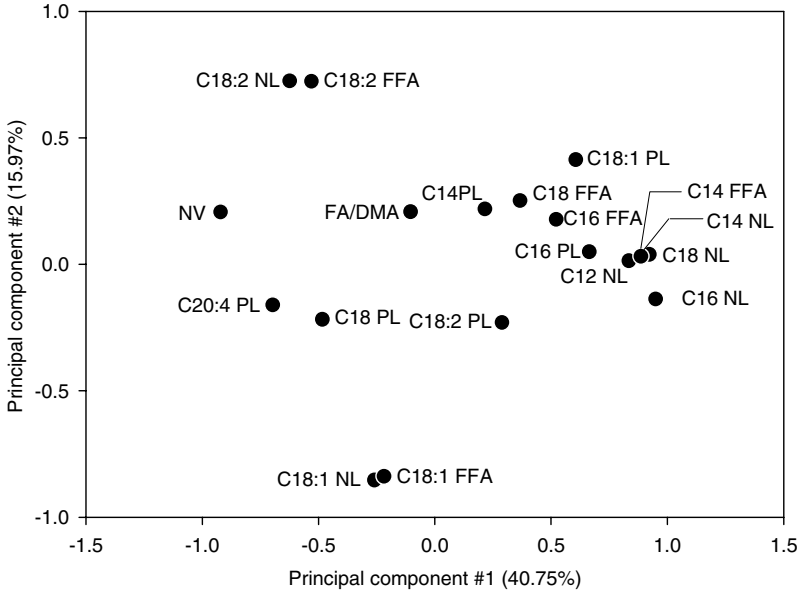

Fig. 1. Loadings plot after principal component analysis of the variables in the plane defined by the two first principal components (PC#1 and PC#2).

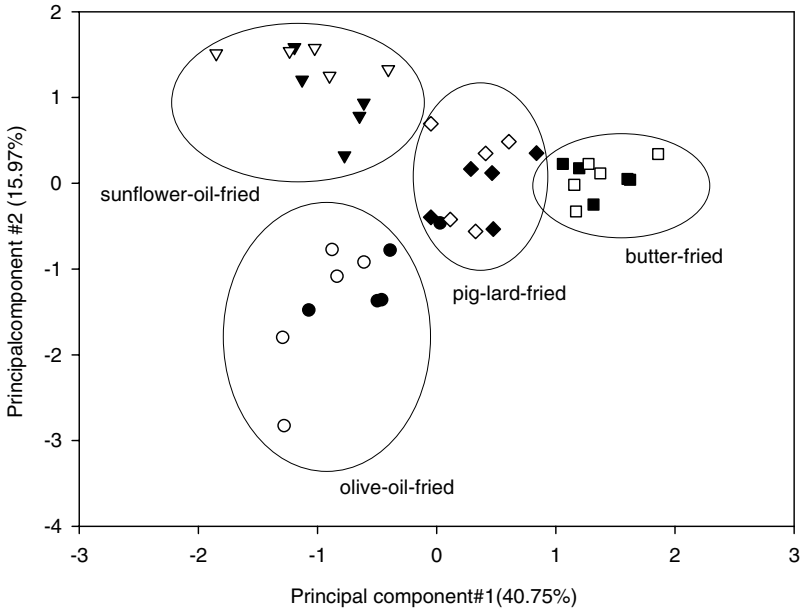

Fig. 2. Scores plot after principal component analysis of the individuals in the plane defined by the two first principal components (PC#1 and PC#2). (Filled figure: day 0, open figure: day 10).

PC#1, in the plane area corresponding to unsaturated fatty acids from NL and FFA fractions, whereas BTLC are grouped to the right with high values of the most saturated fatty acids (C12:0, C14:0 and C16:0) from NL and FFA fractions. PC#2 separates samples fried in sunflower and olive oils, the former being in the positive axis defined by C18:2 and the latter in the negative axis defined by C18:1. Pork loin chops fried in pig lard are grouped near the origin, within the other three groups. The four groups of pork loin chops fried in the different culinary fats may be distinguished through PCA since each one presents a different pattern based on the majority fatty acid profiles of lipid fractions.

4. Conclusion

NL and FFA from pork loin chops fried in olive and sunflower oils, butter and pig lard showed different fatty acids profiles as a result of the exchange between culinary fat and meat. Initial differences were maintained after refrigerated storage due to small changes in fatty acid profiles of lipid fractions from fried samples. These results could be a consequence of frying characteristics that could be related to the inactivating effect of heating on lipolytic enzymes and the protective effect of MRP formed during frying, oxidative processes being the main factors responsible for changes in fatty acids arising during refrigerated storage. The effect of natural antioxidants from oils and heat-induced antioxidants formed during frying in olive oil and sunflower oils could play an important role in protecting unsaturated fatty acids from samples fried in these culinary fats. From a nutritional point of view, frying of meat in olive oil has more beneficial effects than frying in the other culinary fats, due to better fatty acid compositions and fatty acid ratios before and after refrigerated storage.

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