French fries processed with a high content of linolenic acid, low n-6/n-3 ratio and good sensory acceptance after successive frying

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Summary

The objective of this study was to evaluate the stability of the incorporation of linolenic acid in french fries processed with a vegetable oil mixture rich in linolenic acid and with a low ratio between linolenic and linoleic acids (n-6 and n-3). The oil mixture contained 75 % of soybean oil, 20 % of linseed and 5 % of safflower and was compared to soybean oil (control). Potato french fries were subjected to successive frying for 24 h. The french fries were analysed regarding fatty acids composition, tocopherols, sterols and sensory acceptance. During successive frying with the mixture, the french fries were characterized by a higher content of linolenic acid, lower n-6/n-3 ratio, degradation of sterols and by a similar content of tocopherols. The sensory acceptance of the french fries was similar up to 18 h, when the potatoes had a content 2.1-fold higher in linolenic acid, with a 2.7-fold n-6/n-3 ratio, favouring a health-promoting diet.

Keywords

fatty acids; linoleic acid; phytosterols; tocopherols

Vegetable oils and fats, besides granting sensory properties such as aroma, colour and flavour to foods [1], are irrefutable sources of energy, essential fatty acids (EFAs), fat-soluble vitamins, phytosterols, sterols and other important compounds. EFAs are polyunsaturated fatty acids, which cover the n-6 and n-3 families. Their most abundant compounds in nature are linoleic (n-6) and linolenic acid (n-3), which cannot be synthesized by the human organism, making it necessary to be obtained through diet.

EFAs have a broad spectrum of functionality in the human organism and present several health benefits [2]. Considering that the metabolic pathways of the n-6 and n-3 groups are competitive [3, 4], it is essential to ingest the appropriate proportion of these compounds. The recommended ratio for achieving human health benefits is 1 : 1 to 2 : 1 [5]. However, due to dietary changes in the last decades, the level of ingested n-3 decreased, while that of n-6 increased, currently obtaining the ratio between 15 : 1 and 16.7 : 1 [5].

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Although the optimal proportion depends on the level of severity and the pathology in question [6], several studies confirm the importance of linolenic acid and show the need to reinsert it in the diet. A diet containing a low n-6/n-3 ratio was able to reduce risk factors for chronic inflammatory diseases, including cardiovascular and autoimmune diseases, cancer and obesity [7, 8]. The 2.5:1 ratio minimized the proliferation of cancer cells in patients with colorectal cancer, while the 4:1 ratio had no effect. In patients with rheumatoid arthritis, ratios between 2:1 and 3:1 were able to suppress inflammation [6, 9]. The ratio of 5:1 had a beneficial effect on the treatment of asthma, unlike the 10:1 ratio, which demonstrated discordant metabolic effects [10].

Fish, chia seed and linseed are examples of foods rich in n-3, while maize, safflower, canola and sunflower oils are rich in n-6. The soybean oil possesses intermediate amounts of both, but with an n-6/n-3 ratio around 7.6 [11]. Linseed oil was correlated with important pharmacological activities (inhibition of cancer cells proliferation, treatment of diabetes, ulcers and cardioprotective action) that are attributed to the presence of linolenic acid [12]. Similarly, safflower oil was found to be positive in the treatment of neuropathy and control of blood parameters, such as cholesterol and high-density lipoprotein levels, as well as in the improvement of the immune system, which may be associated with its antioxidant properties [13, 14].

MEINHART et al. [15] optimized the composition of an oil mixture for frying french fries based on soybean oil (75 %), safflower oil (5 %) and linseed oil (20 %), whose final product ratio had a high content of polyunsaturated fatty acids and a n-6/n-3 ratio of 2.8, as well as a sensory acceptance similar to that of french fries processed in control oil (pure soybean oil). However, the authors did not study the use of this mixture in successive frying, a process which consists in the continuous use of the oil for several days, accompanied by the replacement of the volume with new oil. During the successive frying of food, fat is continuously exposed to high temperatures in the presence of air. In this process, several reactions occur, ranging from simple nutrient exchanges between the media due to hydrolysis, oxidation and polymerization reactions, altering the nutritional properties (among them degradation of linolenic acid) and sensory properties [12], with odour and taste perception of rancid or fish-like [16].

The objective of this study was to use the previously developed oil mixture (OM) [15], rich in essential fatty acids with a high content of linolenic acid and a low n-6/n-3 ratio, in successive frying of french fries for 24 h in order to investigate the stability of linolenic acid, as well as the general composition of fatty acids, sterols, tocopherols and sensory acceptance.

MATERIALS AND METHODS

Samples and reagents

Refined and recently bottled soybean oil was acquired from Campinas (São Paulo, Brazil). Unrefined safflower and linseed oils, recently processed, were purchased directly from the food industries (Giroil Agroindústria, Entre-Ijuís, Rio Grande do Sul, Brazil). All foods used were free from food preservatives or any additives.

Analytical standards of fatty acid methyl esters (FAME), FAME Mix-37 (18919-1), α, β, χ and δ-tocopherol were obtained from Sigma-Aldrich (Saint Louis, Missouri, USA). Methyl tricosanoate (C23:0) used as an internal standard, stigmasterol, campesterol, cholesterol and β-sitosterol were also from Sigma Aldrich. The FAME solution was prepared in hexane, tocopherols were prepared in hexane containing 0.1 $g \cdot l^{-1}$ of butylated hydroxytoluene (BHT), and the sterols were solubilized in isopropanol. All solutions were mantained at –18 °C and under the absence of light for a maximum of 30 days.

Ethyl ether, acetic acid, chloroform, phenolphthalein, potassium iodide, sodium thiosulfate, starch, ethanol, NaOH, KOH, methanol, hexane, isopropanol and sodium sulfate, all of analytical grade, were obtained from Synth (Diadema, São Paulo, Brazil). Methanol, isopropanol and acetic acid, all in chromatographic grade, were obtained from J. T. Baker (Goiania, Goiás, Brazil). Hexane, chromatographic grade, was obtained from Macron Fine Chemicals (Center Valley, Pennsylvania, USA). BHT was obtained from Sigma Aldrich, BF_3 12% from Merck (Darmstadt, Germany) and NaCl from Allkimia (Campinas, São Paulo, Brazil). Tert-butylhydroquinone (TBHQ) was kindly donated by Danisco (Copenhagen, Denmark). All solutions and samples were filtered through polyvinylidene fluoride membranes with a porosity of 0.22 μm obtained from Millipore (Billerica, Massachussetts, USA).

Frying process and sampling

The successive frying study was performed in a control oil (SO, refined soybean oil, without additives) and in an oil mixture (OM), according to MEINHART et al. [15]. OM was composed

of 750 ml·l^{-1} of refined soybean oil, 200 ml·l^{-1} of unrefined linseed oil and 50 ml·l^{-1} of unrefined safflower oil, added 9 mg of TBHQ for 100 ml of oil, which is lower than the maximum concentration allowed by Brazilian law (20 mg for 100 ml oil) [17]. Pre-fried french fries were purchased in Campinas, Brazil, all from the same batch and from the same supplier.

We used two identical fryers of 2.5 kW electric power (Tedesco, Caxias do Sul, Rio Grande do Sul, Brazil), containing 3.5 l of oil, with a standardized frying procedure as follows: the oil was heated up to 180 ± 2 °C, and then 300 g of frozen french fries were added and fried for 5 min. Then they were left for 2 min at rest to drain the fat. Between the frying sessions, an interval of 5 min was taken to control the oil temperature. The frying procedure was performed uninterruptedly for 6 h and for 4 consecutive days, totalling 24 h of frying. The oil remained at room temperature until the next day, constituting thus a discontinuous successive frying session as it usually occurs in restaurants and snack bars. Before starting the next day's frying session, the oil was filtered and the volume was completed to 3.5 l with fresh oil. At the beginning of each day and at the end of the last day, approximately 100 ml of frying oil from the oil mixture and control were collected for the analysis of acid and peroxide values.

The french fries were analysed for both treatments at the first batches of fries (representing the zero time) and the last batches of each processing day, being equivalent to 6 h, 12 h, 18 h and 24 h of frying. The two batches of french fries withdrawn each time were homogenized, crushed and frozen at –18 °C until the analysis maximum for a maximum of 15 days.

Physico-chemical analyses

For the analysis of the french fries, lipid extraction of the samples was carried out according to the method described by Tabee et al. [18], being used for fatty acids, sterols and tocopherols analyses. Fatty acids were methylated according to the Joseph and Ackman [19]. FAME were analysed using a gas chromatograph Agilent 7890A (Agilent Technologies, Santa Clara, California, USA) equipped with a flame ionization detector. Volumes of 1 μl of samples was injected in a split mode (50:1) at 240 °C. Hydrogen was the carrier gas at a constant flow of 1.4 ml·min^{-1}. Analytes were separated in fused silica capillary column with 90 % of cyanopropyl stationary phase (100 m × 0.25 mm internal diameter × 0.25 μm film thickness; Agilent Technologies). The initial temperature of the column was 197 °C and remained for 23 min, then increased to 225 °C at a rate of 20 °C·min^{-1} and then held for 15 min. The temperature detector was maintained at 240 °C. Identification of the fatty acids was performed by comparing the retention times with those of the analytical standards. Quantification was performed employing the 23:0 standard as a reference.

The analysis of the isomers of tocopherol (α, β, χ and δ-tocopherol) was carried out using a high-performance liquid chromatography system Agilent 1100 (Agilent Technologies) equipped with a fluorescence detector (excitation at 290 nm and emission at 330 nm). The analytes were separated in a normal phase column Hypersil Silica (Thermo Fisher Scientific; Waltham, Massachussetts, USA), 150 mm × 4.6 mm × 3 μm particle size. The mobile phase consisting of hexane : isopropanol : acetic acid (98.9 : 0.6 : 0.5) was used in isocratic conditions with a flow rate of 1 ml·min^{-1}, according to Pinheiro-Sant'Ana et al. [20] and Ballus et al. [21]. Identification of the compounds was performed by comparison with the retention times of the analytical standards and quantification was carried out using external calibration curves.

Extraction of stigmasterol, campesterol, beta-sitosterol and cholesterol was carried out from 0.3 g of oil. The samples were saponified by addition of 10 ml of a KOH 30 g·l^{-1} methanolic solution and then heated in a water bath at 50 °C for 3 h. After cooling down, 10 ml of distilled water were added. The extracts were partitioned with 10 ml of hexane, for 4 times. The organic fractions were joined, evaporated to dryness with nitrogen and then resuspended in 1 ml of isopropanol. A volume of 1 μl of the prepared analytical sample was analysed by gas chromatography as described above for fatty acids, using injection in split mode (for 1 min splitter valve off) at 250 °C. The carrier gas was H_2 at a constant flow of 1.4 ml·min^{-1}. Sterols were separated in an apolar capillary column HP-5 (Agilent Technologies) of (5% phenyl)-methylpolysiloxane (30 m × 0.25 mm × 0.25 μm film thickness). The temperature of the column was held at 150 °C for 0.1 min, with an increase at 20 °C.min^{-1} until 300 °C, and maintaining this temperature for 23 min. The flame ionization detector operated at 300 °C. Identification of the compounds was performed by comparison with the retention times of the analytical standards and quantification was carried out by external calibration curves.

All analyses were performed in triplicate. The chromatographic methods were validated and figures of merit were calculated in accordance

with the requirements of the Brazilian National Health Surveillance Agency (ANVISA) [22] and the recommendations of the International Union of Pure and Applied Chemistry (IUPAC) [23] regarding the detection limits, quantification limits, linear range, accuracy, precision on the day and precision between days.

The oils used in the frying process were evaluated in relation to acidity and peroxide value, also at times 0, 6, 12, 18 and 24 h of frying. The acid value was determined using the method proposed by Adolfo Lutz Institute [24] and the peroxide value was determined according to the AOCS method Cd 8-53 [25]. Other studies of the oil were not performed because well-established data on soybean oil are already available in the literature, while for the mixture, MEINHART et al. [15] already demonstrated good stability through oxygen induction assays.

Sensory analysis

Twenty-nine volunteer consumers were recruited for the sensory analysis of samples during four consecutive days, always at the same time. Among the volunteers, 72 % were female and 28 % were male; 83 % were between 18 and 30 years of age, 14 % were between 31 and 40 years of age, and 3 % were more than 51 years of age; 24 % reported consuming french fries weekly, 21 % fortnightly and 55 % monthly.

Approximately 30 g of french fries prepared with both oils were served to the consumers, without the addition of salt. The samples were 3-digits coded and randomly presented to consumers in individual cabins (air-conditioned at 22 °C), under monochromatic light, in white or transparent disposable vessels. Samples were evaluated by each consumer in a monadic order, the order of presentation following a complete balanced design as described by STONE et al. [26]. Between each sample analysis, a biscuit was provided to eat and water to drink.

The study involved sensory acceptance testing with mixed structured hedonic scale (ranging from 1 – I disliked very much to 9 – I liked very much) for the attributes colour, aroma, flavour, texture and overall impression. At the same analysis, a scale test was applied in relation to the ideal (colour, aroma, flavour and crispness) and purchase intent with mixed hedonic structured scale (ranging from 1 – I would certainly buy it to 5 – I would certainly not buy it).

Statistical analyses

The results of the physico-chemical analyses and those of the acceptance test were analysed using the ANOVA test, and the average values were compared using the Tukey's test ($p < 0.05$) by Statistica 7.0 (Statsoft, Tulsa, Oklahoma, USA) and SAS software (SAS, Cary, North Caroline, USA). The correlation between physico-chemical and sensory results was tested by principal component analysis (PCA), using the software Pirouette (Infometrix; Bothell, Washington, USA). In order to carry out this analysis, data were autoscaled to have the same magnitude of response (average equal to zero and standard deviation equal to one).

RESULTS AND DISCUSSION

The results of the analytical method validation for the figures of merit are shown in Tab. 1. These data were in agreement with ANVISA and IUPAC [22, 23] indicating that the methods were suitable for carrying out the analyses in question. Tab. 2 shows the composition of fatty acids, sterols and tocopherols in french fries obtained from both treatments, SO and OM.

Regarding sterols, β-sitosterol was the major compound in both treatments, as previously reported by CHIOU et al. [27] on french fries processed with soybean, sunflower and palm oils. Among the formulations, it was possible to observe that the content of β-sitosterol in french fries was reduced by 13 % and 18 % for SO and OM, respectively, during the 24 h of frying. The degradation of stigmasterol represented 25 % and 28 % for SO and OM respectively, while that of campesterol was 27 % and 32 % for SO and OM, respectively. No difference was observed for cholesterol. Such reduction in the contents of phytosterols may be related to chemical degradation of these compounds by thermal processing. IGOUMENIDIS et al. [28] evaluated the kinetics of sterol degradation in vegetable oils and potatoes submitted to frying, and also found a decrease in the content of these compounds, attributed to oxidation during thermal processing, leading to formation of oxysterols. Under other heating conditions, degradation was also observed. Using microwave heating, LEAL-CASTAÑEDA et al. [29] found that during the first 1.5 min, degradation of 30 % of sterols took place and then their content remained constant until 6 min of heating. After 30 min of heating, only 24 % of the initial sterol content was observed. MENENDEZ-CARREÑO et al. [30] observed degradation of 38 % of stigmasterol after heating at 180 °C for 1 h in a Termaks oven (Termaks, Bergen, Norway).

Among the tocopherols, χ-tocopherol was the major compound in the french fries in both treat-

Tab. 1. Figures of merit obtained from method validation procedures used in tocopherols isomers, phytosterols and fatty acids determinations.

Parameters		Tocopherols				Phytosterols				Fatty acids
		α	β	χ	δ	Cholesterol	Campesterol	Stigmasterol	β-Sitosterol	
Intra-day precision [%] (n = 10)	Level 1	1.0	1.2	1.6	1.0	0.4	0.6	0.9	1.3	< 4.6
	Level 2	1.2	1.0	0.9	0.8	2.3	1.2	1.7	2.4	< 6.8
	Level 3	3.5	4.4	4.4	4.4	2.3	2.4	2.0	6.5	< 5.5
Inter-day precision [%] (n = 3)	Level 1	1.5	1.5	1.9	1.0	1.0	0.8	0.9	1.2	< 5.9
	Level 2	1.2	0.9	0.9	1.0	0.7	0.9	0.7	1.5	< 5.2
	Level 3	2.7	1.9	2.8	2.2	1.9	3.0	3.3	8.4	< 5.8
Accuracy [%]	Level 1	104.0	92.3	101.0	107.3	103.1	107.4	94.5	102.8	–
	Level 2	100.4	94.5	100.5	103.5	97.5	104.1	101.8	95.2	–
	Level 3	103.2	96.9	102.8	105.5	102.8	94.5	103.2	98.4	–
Linear range [mg·l^{-1}]		0.08–20.00	0.03–20.00	0.03–20.00	0.01–20.00	1.63–10.00	1.84–10.00	2.47–10.00	3.52–10.00	2.00–10.00
Detection limit [mg·l^{-1}]		0.04	0.02	0.02	0.00	0.82	0.92	1.23	1.76	< 1.02
Quantification limit [mg·l^{-1}]		0.08	0.04	0.03	0.01	1.64	1.84	2.47	3.53	< 2.04

Precision values are expressed as relative standard deviation.
Level 1 – quantification limit, Level 2 – intermediate concentration of the linear range, Level 3 – maximum concentration of the linear range. Linear range with adjustment of the models, considering the critical F value with 95% confidence, with curves performed with 6 concentrations in random triplicate.

ments during up to 12 h of frying. This observation agreed with that of Anwar et al. [31]. A reduction in β, χ and δ-tocopherol levels during the frying time was observed, which may be associated with degradation of these compounds under the frying conditions. When comparing the different treatments, it was observed that during 24 h of frying, the french fries processed with SO and OM had similar degradation for the β-tocopherol (91 % and 96 % for SO and OM, respectively), χ-tocopherol (98 % for both) and δ-tocopherol (79 % and 76 % for SO and OM, respectively). Different results were obtained for α-tocopherol, where no degradation occurred for the SO formulation and 24% degradation occurred for the OM formulation. Wagner et al. [32], when evaluating the antioxidant effects of α, χ and δ-tocopherols in lipid emulsions, found that α-tocopherol had the lowest lipid oxidation-minimizing effect, corroborating with the data observed in the present study. Hashemi et al. [33] also found that the total tocopherols content in new sources of edible oils was reduced after 15 min of microwave heating, reducing the oxidative stability of the seed oils.

The most abundant fatty acids in french fries processed with soybean oil were palmitic acid (16:0), oleic acid (18:1) and linoleic acid (18:2), corroborating the data reported in the literature by Tabee et al. [18]. The content of n-3 fatty acids was higher in french fries processed with the OM formulation compared to SO at all frying times. In SO formulation, n-6 levels were higher than those in OM formulation at all frying times. The n-6/n-3 ratios were approximately 2.6-fold lower at all frying times in french fries processed with OM. This aspect shows that the oil mixture had a nutritional balance favourable from the aspect of a health-supporting diet [5]. The levels of the sum of polyunsaturated fatty acids were reduced in both formulations as the hours of frying advanced.

The acid and peroxide values of the oils were lower than 520 mg·kg^{-1} and 0.093, respectively, for all frying times. These values were in accordance with the limits established by Brazilian legislation [34].

The results of the sensory study are shown in Tab. 3. Samples of french fries from both treatments did not differ (with 95% of confidence) between each other at all times of frying for colour, flavour, aroma, texture and overall impression in the acceptance test. In the ideal test, the percentage of tasters who provided

Tab. 2. Contents of fatty acids, sterols and tocopherols in oils during the successive frying process.

Compounds	Soybean oil				
	0 h	6 h	12 h	18 h	24 h
Fatty acids [g·kg^{-1}]					
16:00	14578.6 ± 191.4^{bA}	15815.9 ± 547.8^{aA}	13963.8 ± 93.6^{bA}	12847.5 ± 403.5^{cA}	12341.5 ± 321.9^{cA}
17:00	737.5 ± 88.8^{aA}	1035.7 ± 71.3^{aA}	859.7 ± 75.9^{aA}	781.4 ± 195.4^{aA}	769.9 ± 178.9^{aA}
18:00	5352.7 ± 76.8^{bcA}	6194.1 ± 128.7^{aA}	5675.5 ± 130.6^{bA}	5086.3 ± 246.3^{cA}	5100.8 ± 274.2^{cA}
18:1 n-9	34438.3 ± 521.7^{cB}	47775.7 ± 1510.6^{bB}	50262.3 ± 1094.1^{bA}	49408.7 ± 1367.4^{bA}	55563.1 ± 904.6^{aA}
18:2 n-6	73873.2 ± 1214.6^{aA}	74352.7 ± 2893.3^{aA}	61297.8 ± 437.7^{bA}	54753.4 ± 1629.9^{cA}	49897.8 ± 1072.1^{dA}
18:3 n-3	10248.7 ± 190.7^{aB}	9708.3 ± 413.9^{aB}	7682.5 ± 138.9^{bB}	6704.9 ± 221.2^{cB}	5841.7 ± 190.2^{dB}
SFA	20668.7 ± 302.6^{bA}	23045.6 ± 647.6^{aA}	20499.0 ± 251.3^{bA}	18715.2 ± 748.8^{cA}	18212.1 ± 763.3^{cA}
PUFA	84121.9 ± 1397.7^{aA}	84061.0 ± 3303.5^{aA}	68980.3 ± 570.2^{bA}	61458.3 ± 1821.8^{cA}	55739.5 ± 1260.8^{dA}
n-6/n-3	7.2 ± 0.0^{dA}	7.7 ± 0.1^{cA}	8.0 ± 0.1^{bA}	8.2 ± 0.1^{bA}	8.5 ± 0.1^{aA}
Sterols [mg·kg^{-1}]					
Cholesterol	2.0 ± 0.1^{aA}	1.6 ± 0.0^{cdB}	1.9 ± 0.0^{abA}	1.4 ± 0.1^{dB}	1.7 ± 0.1^{bcA}
Campesterol	44.9 ± 1.5^{aB}	45.0 ± 2.3^{aB}	42.9 ± 1.6^{aA}	34.7 ± 1.5^{bB}	33.0 ± 2.1^{bA}
Stigmasterol	72.0 ± 3.2^{aA}	72.7 ± 3.7^{aA}	69.0 ± 2.4^{aA}	56.7 ± 2.3^{bA}	54.2 ± 3.7^{bA}
β-Sitosterol	279.2 ± 13.1^{abA}	289.6 ± 15.9^{aB}	290.2 ± 10.6^{aA}	239.7 ± 10.0^{cA}	244.0 ± 17.1^{bcA}
Tocopherols [mg·kg^{-1}]					
α	23.6 ± 0.9^{bA}	27.0 ± 0.4^{aB}	24.5 ± 1.3^{bA}	23.0 ± 0.5^{bA}	24.1 ± 1.1^{bA}
β	4.4 ± 0.0^{aB}	2.6 ± 0.1^{bB}	1.0 ± 0.0^{cA}	0.6 ± 0.0^{dB}	0.4 ± 0.0^{eA}
χ	109.9 ± 5.8^{aA}	44.3 ± 0.7^{bB}	11.9 ± 0.1^{cA}	5.5 ± 0.3^{cdB}	2.1 ± 0.1^{dA}
δ	8.4 ± 0.5^{aA}	6.1 ± 0.1^{bA}	4.5 ± 0.2^{cA}	2.8 ± 0.1^{dA}	1.8 ± 0.1^{eA}

Compounds	Oil mixture				
	0 h	6 h	12 h	18 h	24 h
Fatty acids [g·kg^{-1}]					
16:00	12183.8 ± 75.2^{bB}	14998.8 ± 465.6^{aA}	11124.3 ± 145.9^{bB}	11249.7 ± 910.2^{bB}	9619.5 ± 109.2^{cB}
17:00	681.7 ± 95.9^{cA}	1009.8 ± 88.3^{abA}	736.6 ± 38.1^{bcA}	1039.0 ± 204.1^{aA}	819.0 ± 2.0^{abcA}
18:00	5193.5 ± 91.7^{bcA}	6546.9 ± 231.2^{aA}	4523.5 ± 82.7^{dB}	5368.6 ± 361.3^{bA}	4669.9 ± 83.1^{cdA}
18:1 n-9	37231.4 ± 215.7^{bA}	53591.8 ± 1319.1^{aA}	50083.8 ± 701.4^{aA}	50819.8 ± 5089.6^{aA}	48184.0 ± 602.8^{aB}
18:2 n-6	58755.3 ± 149.5^{bB}	66318.3 ± 1621.5^{aB}	44514.9 ± 683.8^{cB}	44173.7 ± 4123.3^{cB}	37122.2 ± 557.4^{dB}
18:3 n-3	21692.8 ± 133.3^{aA}	23422.7 ± 654.5^{aA}	15707.9 ± 531.7^{bA}	14345.5 ± 1450.0^{bA}	11642.1 ± 246.5^{cA}
SFA	18058.9 ± 233.8^{bB}	22555.4 ± 778.0^{aA}	16384.4 ± 234.9^{bcB}	17657.3 ± 1295.3^{bA}	15108.3 ± 106.1^{cB}
PUFA	80448.1 ± 180.9^{bB}	89741.0 ± 2261.2^{aA}	60222.7 ± 1198.5^{cB}	58519.2 ± 5569.0^{cA}	48764.2 ± 803.6^{dB}
n-6/n-3	2.7 ± 0.0^{dB}	2.8 ± 0.0^{cB}	2.8 ± 0.1^{cB}	3.1 ± 0.0^{bB}	3.2 ± 0.0^{aB}
Sterols [mg·kg^{-1}]					
Cholesterol	2.1 ± 0.1^{abA}	2.3 ± 0.1^{aA}	1.6 ± 0.1^{cB}	1.7 ± 0.1^{cA}	1.8 ± 0.1^{bcA}
Campesterol	53.2 ± 2.6^{bA}	61.0 ± 3.6^{aA}	33.3 ± 0.9^{dB}	39.9 ± 0.6^{cA}	36.3 ± 1.4^{cdA}
Stigmasterol	65.3 ± 3.4^{bA}	76.0 ± 4.1^{aA}	54.2 ± 2.9^{cB}	50.2 ± 2.0^{cA}	47.1 ± 1.2^{cB}
β-Sitosterol	285.6 ± 15.5^{bA}	341.0 ± 24.5^{aA}	246.2 ± 7.6^{cB}	253.1 ± 2.5^{bcA}	233.0 ± 9.4^{cA}
Tocopherols [mg·kg^{-1}]					
α	24.2 ± 0.2^{bA}	30.5 ± 0.9^{aA}	19.1 ± 1.1^{cB}	23.2 ± 0.7^{bA}	18.5 ± 0.4^{cB}
β	7.0 ± 0.1^{aA}	4.2 ± 0.2^{bA}	0.3 ± 0.0^{dB}	0.7 ± 0.0^{cA}	0.3 ± 0.0^{dB}
χ	87.8 ± 1.1^{aB}	49.1 ± 2.7^{bA}	2.1 ± 0.1^{dB}	6.1 ± 0.2^{cA}	1.9 ± 0.0^{dB}
δ	5.8 ± 0.1^{aB}	5.5 ± 0.3^{aB}	1.5 ± 0.1^{cB}	2.5 ± 0.2^{bB}	1.4 ± 0.1^{cB}

Values represent average ± standard deviation (n = 3). Lowercase letters indicate the differences among the different times, for the same formulation. Uppercase letters indicate the differences among the formulations, for the same time (with 95% confidence).
SFA – saturated fatty acids, PUFA – polyunsaturated fatty acids.

scores between –1.5 and 1.4 (scale considered as ideal) was similar between the formulations for aroma, colour and texture attributes, with variations of a maximum of 10 % for aroma, 7 % for colour and 4 % for texture. For flavour, although no significant difference was observed between the formulations, it was observed that after 18 h, the frequency of tasters who judged the SO french fries close to the ideal, was by 17 % higher compared to OM ones. The differences observed by the tasters (within 24 h of frying) were possibly related to lipid oxidation, which is more intense in oils with higher contents of polyunsaturated fatty acids. It should be noted that the linseed and safflower oil used in OM were not refined and thus contained tocopherols and sterols, which are antioxidants, but also contained compounds catalysing oxidation [3, 35].

Up to 18 h of frying, no significant difference was observed between the OM and SO formulations. In this frying time, a consumer who ingests the fried product with OM obtains a 2.1-fold increase in linolenic acid with 2.7-fold lower n-6/n-3, favouring a healthier diet, with degraded tocopherols and phytosterols. Thus, the successive frying time of 18 h can be considered as the maximum, since foods with a high content of linolenic and/or polyunsaturated acid are reported as negatively influencing the sensorial attributes due to the development of rancid or fish-like flavours and odours [16].

In data exploratory analysis, the data matrix containing 10 samples and 20 variables (including the variables of the physico-chemical and sensory analysis) was used for PCA. We observed that, with the first two principal components, it was possible to explain 72.3 % of the total variance of the data (Fig. 1) and to visualize the nutritional changes and sensory perceptions of french fries processed with OM and SO. The first prin-

Tab. 3. Results of sensory evaluation of french fries.

Attributes and scales		Soybean oil				Oil mixture			
		6 h	12 h	18 h	24 h	6 h	12 h	18 h	24 h
Similarity between formulations									
Aroma		7.42	7.22	6.95	7.25	7.43	7.43	7.15	7.27
Flavour		6.49	7.09	6.52	6.89	7.04	7.02	6.63	6.34
Texture		6.70	6.93	6.59	6.75	7.10	6.65	6.54	6.62
Colour		7.39	7.38	7.02	7.21	7.76	7.58	6.95	7.03
Overall impression		7.00	7.23	6.64	7.03	7.49	7.07	6.81	6.72
Frequency of scale in relation to the ideal (0)									
Flavour	–4.5 to –1.5	7 %	7 %	7 %	0 %	7 %	7 %	14 %	17 %
	–1.5 to 1.4	83 %	93 %	86 %	93 %	79 %	90 %	83 %	76 %
	1.5 to 4.5	10 %	0 %	7 %	7 %	14 %	3 %	3 %	7 %
Aroma	–4.5 to –1.5	3 %	3 %	10 %	0 %	0 %	3 %	3 %	7 %
	–1.5 to 1.4	90 %	97 %	83 %	90 %	93 %	93 %	93 %	93 %
	1.5 to 4.5	7 %	0 %	7 %	10 %	7 %	3 %	3 %	0 %
Colour	–4.5 to –1.5	0 %	3 %	3 %	3 %	3 %	0 %	7 %	3 %
	–1.5 to 1.4	93 %	97 %	86 %	83 %	86 %	100 %	86 %	90 %
	1.5 to 4.5	7 %	0 %	10 %	14 %	10 %	0 %	7 %	7 %
Texture	–4.5 to –1.5	10 %	10 %	14 %	14 %	7 %	14 %	14 %	14 %
	–1.5 to 1.4	79 %	90 %	83 %	79 %	79 %	86 %	83 %	86 %
	1.5 to 4.5	10 %	0 %	3 %	7 %	14 %	0 %	3 %	0 %
Frequency of purchase intent									
1 – I would certainly buy		41 %	31 %	17 %	24 %	45 %	31 %	31 %	31 %
2 – I would probably buy		38 %	55 %	41 %	45 %	41 %	45 %	41 %	28 %
3 – I doubt if I would buy		10 %	7 %	38 %	24 %	10 %	21 %	21 %	28 %
4 – I probably would not buy		10 %	7 %	14 %	7 %	3 %	3 %	3 %	7 %
5 – I certainly would not buy		0 %	0 %	0 %	0 %	0 %	0 %	3 %	7 %
Sum (1 and 2)		79 %	86 %	59 %	69 %	86 %	76 %	72 %	59 %

According to the Tukey's test (95% confidence), there was no difference among the different times (of each formulation), not even between both formulations at the same time.

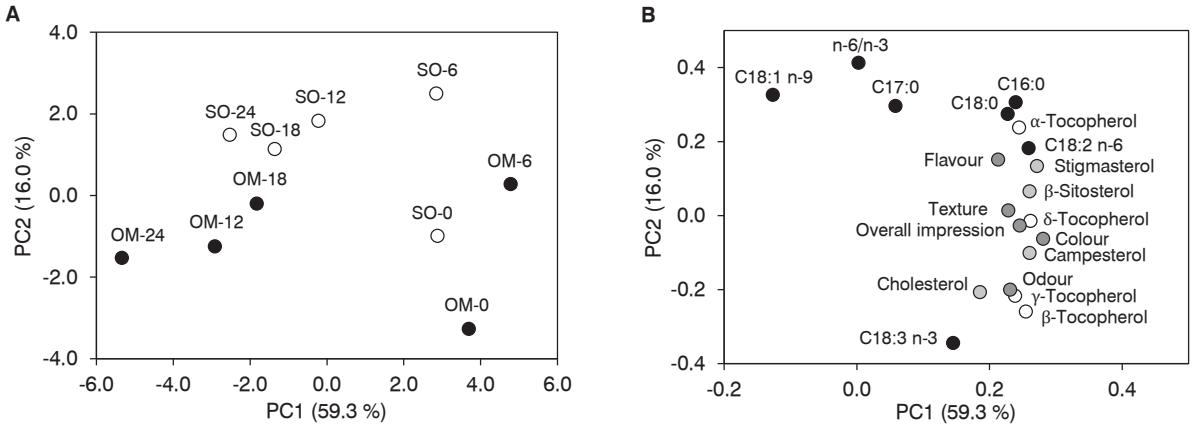

Fig. 1. Principal components analysis of oils during the successive frying process.

A – Score plots, B – loading plots.
SO-0, SO-6, SO-12, SO-18 and SO-24 – soybean oil at sucessive frying times of 0, 6, 12, 18 and 24 h, respectively.
OM-0, OM-6, OM-12, OM-18, OM-24 – oil mixture at sucessive frying times of 0, 6, 12, 18, 24 h, respectively.

cipal component (PC1) showed that most of the variables, among them 18:2 n-6, sterols, tocopherols and sensory attributes of acceptance, were highly correlated with the samples processed at time 0 h and 6 h of frying. Oleic acid, in contrast to most of the variables, was positively correlated with the increase of the frying time for both treatments, which occurred possibly due to oxidation of polyunsaturated fatty acids.

In the second principal component (PC2), the variables n-6/n-3 ratio and 18:3 n-3 were responsible for discriminating the samples processed with SO and OM in all frying times. French fries from OS showed the highest score in comparison with the french fries processed with the mixture for n-6/n-3 ratio and the highest score of french fries with the oil mixture was 18:3 n-3. Thus, the nutritional gain of french fries with the mixture processed for up to 18 h was evident, but from that moment on, we observed a reduction in sensory acceptance, considering the test in relation to the ideal for flavour and the evaluation of purchase intent.

CONCLUSIONS

The study showed that the content of linolenic and linoleic acid, sterols and tocopherols decreased in both treatments over the frying time. Samples fried with the oil mixture (75 % of soybean oil, 20 % of linseed oil and 5 % of safflower) had twice the content of linolenic acid and 2.6-fold lower n-6/n-3 ratio during 24 h of frying. Degradation of phytosterols and tocopherols was little influenced by the formulations. Up to 18 h of frying, evaluators did not notice a significant sensorial difference. These data show that the use of the oil mixture resulted in a nutritionally better products than that obtained by frying with 100% soybean oil. Such product presents a new alternative for enriching the human diet.

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