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A study by ^{1}H nuclear magnetic resonance of the influence on the frying medium composition of some soybean oil-food combinations in deep-frying

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ABSTRACT

A study of the evolution of the composition of both soybean oil submitted to heating at frying temperature for a prolonged period of time, as well as of soybean oil-frying media used in three different series of deep-frying experiments is carried out by means of ^{1}H nuclear magnetic resonance. The foods involved in the deep-frying processes have very different lipid contents and their lipid composition is also very different. The results obtained allow one to clarify how the nature of the food being fried influences the changes observed in the composition of the soybean oil-frying media throughout the deep-frying process. The study refers both to the evolution of the molar percentage of the different kinds of acyl groups in the frying-media as well as to the nature of the aldehydes formed and the evolution of their concentrations. It is noteworthy that the main aldehydes detected, in both soybean oil and soybean oil-frying media, are the reactive (*E,E*)-2,4-alkadienals; likewise the genotoxic and cytotoxic 4-hydroxy-(*E*)-2-alkenals and 4,5-epoxy-2-alkenals are also present. The considerable influence of the food being fried on the occurrence of these reactive and toxic aldehydes in the frying media is shown. Furthermore, the occurrence and evolution of other oxygenated compounds such as alcohols are also addressed, as is the extent of hydrolytic processes. In addition, the evolution of Iodine Value and of the percentage in weight of Polar Compounds is also considered. The influence of the oil nature on all the above mentioned compositional characteristics is also given attention by comparison of these results with those previously obtained using extra virgin olive oil; it is noteworthy that from the toxic aldehyde content point of view the results obtained indicate that the extra virgin olive oil-frying media are much safer than the soybean oil-frying media.

1. Introduction

Soybean oil behavior in frying experiments has been the subject of several papers. In some cases the aim of the study was to compare the performance of soybean oils of different content in linoleic groups, or of mixtures with more saturated oils (Abdulkarim, Long, Lai, Muhammad, & Ghazali, 2007; Gerde, Hardy, Fehr, & White, 2007; Kupongsak & Kansuwan, 2012; Machado, Marmesat, Abrantes, & Dobarganes, 2007; Mounts, Wamer, List, Neff, & Wilson, 1994; Normand, Eskin, & Przybylski, 2003; Tompkins & Perkins, 2000; Tseng, Moreira, & Sun, 1996; Warner & Fehr, 2008; Warner & Gupta, 2003). French fries, potato chips, and tortillas were often the foods involved in these studies, and the evaluation of the oil degradation level was carried out by classical methods such as changes in color, in viscosity, free fatty acids, Peroxide Value, p-Anisidine Value, Iodine Value, Specific Extinction at 233 and 269 nm or total Polar Compounds.

Studies in which the identification and quantification of secondary oxidation compounds are addressed are much more scarce. However, the evaluation of the emission rates of certain carbonyl compounds during soybean oil heating at frying temperature has been carried out (Da Silva & Pereira, 2008). Nevertheless, the carbonyl compounds that remain in the oil after heating are of much greater interest. Specifically in the case of soybean oil, the formation and content of some oxygenated *alpha,beta*-unsaturated aldehydes after heating at high temperature or after frying have been reported (Gerde, Hammond, & White, 2011; Han & Csallany, 2008; Seppanen & Csallany, 2001, 2002, 2004, 2006).

The evolution of oil degradation as well as the formation of primary and secondary oxidation compounds in thermal experiments is highly dependent on all the factors involved in the process, which include the amount of oil, air-oil contact surface, temperature, oil nature, etc.

In this study the evolution of the soybean oil composition at frying temperature in an industrial fryer is analyzed from data coming from its ^{1}H NMR spectra registered at regular intervals of time throughout the heating experiment; attention is paid both to the degradation of oil acyl groups and to the formation of new functional groups. This technique has not been previously used in the study of the soybean oil degradation at frying temperature. The study also covers the evolution of the soybean oil-frying media composition in three series of deep-frying experiments of three foods of very different compositions. This will provide information on the influence of food nature on the

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performance of soybean oil in deep-frying and, in addition, may contribute to the search for the best food-oil combinations to obtain safer and healthier fried foods. In spite of their importance these two latter aims have received little attention until now.

2. Materials and methods

2.1. Oil and food samples

The oil used in this study was soybean oil, acquired in a local supermarket. Its composition in molar percentages of linolenic (Ln), linoleic (L), oleic or monounsaturated (O or MU) and saturated (S) acyl groups was 4.4, 53.0, 27.9 and 14.7 respectively; this was determined from the ^{1}H NMR spectrum as in previous studies (Guillén & Uriarte, 2012a).

The foods submitted to deep-frying were: commercial dough for making Spanish doughnut (estimated average composition: water 29.6%, proteins 8.0%, carbohydrates 60.8% and lipids 0.8%), pork adipose tissue (estimated average composition: water 18.0%, proteins 4.7%, and lipids 76.7%), and farmed salmon fillets (*Salmo salar*) (estimated average composition: water 55.5%, proteins 17.6%, and lipids 26.2%). All of them were also acquired in local supermarkets and were defrosted before frying. Both the lipidic content of these foods and their lipidic composition are very different (lipids of Spanish doughnut dough: Ln 4.0%, L 55.0%, O 15.5% and S 21.5%; lipids of pork adipose tissue: Ln 1.5%, L 9.5%, O 48.6%, and S 40.4%; lipids of farmed salmon fillets: omega-3 groups, (ω-3) 19.0%, L 9.4%, O or monounsaturated (MU) 51.3% and S 19.7%); this was determined, in the case of pork adipose tissue and of farmed salmon fillets, by ^{1}H NMR as in previous studies (Guillén & Uriarte, 2012a; Vidal, Manzanos, Goicoechea, & Guillén, 2012), after extraction using ultrasound and carbon disulfide as solvent. It should also be noticed that the omega-3 groups of these salmon lipids contain 5.5 ± 1.1% of docosahexaenoic (DHA) acyl groups and 5.9 ± 1.1% of eicosapentaenoic (EPA) acyl groups. The lipidic composition of the dough was calculated from its formulation, taking into account the composition of wheat flour.

2.2. Heating of the soybean oil at frying temperature and deep-frying experiments

In both the soybean oil heating and the three series of deep-frying experiments, 4 L of soybean oil was used; these were placed in an industrial fryer (Franke ECO4, 230 V, 10A, 2.3 kW) and submitted at 190 °C (frying temperature) for periods of 8 h/day, for 4 days, storing the oil and the frying medium between these periods at room temperature. The total heating time was 32 h and 30 min, and 14 frying experiments were carried out in each one of the three series of deep-frying experiments; the first frying experiment in each series was undertaken exactly when the oil reached 190 °C, and the subsequent frying experiments at regular intervals of 2.5 h. A metallic basket was used for the introduction of the foods into the oil and to remove them. The deep-frying time was in all cases 1 min. In the case of the Spanish doughnut each frying experiment was carried out with eight pieces of defrosted dough shaped into cylinders 10 cm in length and 1 cm in diameter, weighing 40 g in total. In the cases of pork adipose tissue and salmon fillets, six pieces (7 cm by 3 cm by 1.75 cm of pork adipose tissue) and four pieces (7 cm by 5 cm by 3 cm of salmon fillet), weighing in total 250 g, were fried simultaneously in each frying experiment. During each series of deep-frying experiments no oil was replenished. The dimensions of the stainless steel tank of the fryer were 15 cm wide × 30 cm long × 17 cm high. During heating or frying no amount of oil was replenished and the temperature was periodically tested by a calibrated thermometer. Oil and frying medium samples were taken at intervals and, when necessary, refrigerated until their study in order to avoid or hinder the continuation of the degradation process. Oil heating and the series of deep-frying experiments using dough and pork adipose tissue were carried out in duplicate, and the series of deep-frying salmon experiments in triplicate. The soybean oil submitted to heating at frying temperature was named SB, and the frying media involved in the deep-frying of Spanish doughnut dough, pork adipose tissue and salmon fillets were named DSB, PSB and SSB respectively.

2.3. Monitoring of the composition of the frying media evolution by ^{1}H nuclear magnetic resonance spectroscopy

The evolution of the composition of soybean oil submitted to heating at frying temperature and of the frying media involved in several series of deep-frying experiments was monitored by ^{1}H nuclear magnetic resonance. To this aim, the ^{1}H nuclear magnetic resonance spectra of both the original soybean oil, and the frying medium throughout the several experiments (heating and frying experiments), were registered in a Bruker Avance 400 spectrometer operating at 400 MHz. The oil sample (200 μl) was mixed in a 5 mm diameter tube with 400 μl of deuterated chloroform which contained 0.2% of non deuterated chloroform and a small amount (0.03%) of tetramethylsylane (TMS) as internal references. In order to select the most appropriate values to obtain accurate quantitative results in the smallest possible period of time, a very broad range of recycling times and relaxation delays were tested in the acquisition of the ^{1}H NMR spectra, not only of the original oil but also of the oil submitted to heating or frying. As a result of these tests, the acquisition parameters used were: spectral width 6410 Hz, relaxation delay 3 s, number of scans 64, acquisition time 4.8190 s, and pulse width 90°, with a total acquisition time of 8 min 38 s. The experiment was carried out at 25 °C. The spectra of the lipids of the raw pork adipose tissue and salmon fillets used in this study were also acquired in the same way.

The ^{1}H NMR spectra of the original oil and of the oil (SB) and frying media (DSB, PSB and SSB) after 32.5 h of heating or 14 frying experiments respectively are shown in Fig. 1. Table 1 shows the assignment of the main signals of these spectra, their multiplicities and coupling constants; the meaning of some of the abbreviations indicated in Table 1 is the following: s, singlet; d, doublet; t, triplet; m, multiplet; and dd, double doublet. Some of these signals were assigned as in previous studies (Guillén & Ruiz, 2003a,b, 2005a,b,c; Guillén & Uriarte, 2012a; Sopelana, Arizabaleta, Ibargoitia, & Guillén, 2013; Vidal et al., 2012) and the assignment of other signals has been undertaken in this paper for the first time. The areas of the ^{1}H NMR signals are proportional to the number of protons which generate each signal; for this reason quantitative results can be obtained from the ^{1}H NMR spectral data. Each sample was analyzed in triplicate and the data used in this study are average values.

In this study triolein, tristearin, trilinolein and trilinolenin, as well as oleic and linoleic acids and some primary and secondary alcohols ((*E*)-2-penten-1-ol and 1-octen-3-ol) (all of them acquired from Sigma Aldrich (St. Louis, MO, USA)) as well as aldehydes of different types (heptanal, octanal, (*E*)-2-heptenal, (*E*)-2-octenal, (*E,E*)-2,4-heptadienal, (*E,E*)-2,4-nonadienal, (*E,E*)-2,4-decadienal, 4-hydroxy-(*E*)-2-hexenal and 4-hydroxy-(*E*)-2-nonenal) (acquired from Cayman Chemical (Ann Arbor, MI, USA), and Sigma Aldrich (St. Louis, MO, USA)) and certain 1,2-diglycerides, and 1,3-diglycerides (1,2-dioleoylglycerol, 1,3-dioleoyl-rac-glycerol and dipalmitin) (acquired from Sigma Aldrich, (St. Louis, MO, USA)), were used as standard compounds for both the assignment of certain signals of the spectra and for quantitative purposes.

Using the area of certain signals of the spectra, indicated in Fig. 1 and assigned in Table 1, the molar percentage of the several kinds of acyl groups in the oil throughout the heating and in the frying media through the three series of deep-frying experiments was determined as in previous studies (Guillén & Uriarte, 2012a,b). The equations used for this purpose were the following: molar percentage of linolenic groups, $Ln = 100\ (A_{JLn} / 3A_N)$ Eq. (1); molar percentage of linoleic groups, $L = 100\ (2A_{JL} / 3A_N)$ Eq. (2); molar percentage of oleic (or monounsaturated) groups, O (or MU) $= 100\ [(A_H - 2A_{JL} - A_{JLn}) / 3A_N]$ Eq. (3); and molar percentage of saturated plus modified acyl groups, $(S + M) = 100\ [1 - (A_H / 3A_N)]$ Eq. (4). In these equations A_{JLn} and A_{JL} are the areas of the signals of *bis*-allylic protons of linolenic