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Analytical Methods

Deep-frying food in extra virgin olive oil: A study by ^{1}H nuclear magnetic resonance of the influence of food nature on the evolving composition of the frying medium

Andrea Martínez-Yusta, María Dolores Guillén *

Food Technology, Faculty of Pharmacy, Lascaray Research Center, University of the Basque Country (UPV-EHU), Paseo de la Universidad No. 7, 01006 Vitoria, Spain

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ABSTRACT

Three series of fourteen deep-frying experiments on three foods of very different compositions were carried out using extra virgin olive oil as the original frying medium. The aim of the study was to establish how the nature of the food being fried influences the composition of the frying medium. The changes in the composition of the frying media referred to the evolution of molar percentage of the different kinds of acyl groups, as well as to the evolution of the concentration of newly formed compounds such as aldehydes, epoxystearyl groups, primary and secondary alcohols were monitored in a simultaneous way by ^{1}H NMR spectroscopy. Changes due to hydrolytic processes were also considered. In addition, the evolution of the Iodine Value and percentage in weight of polar compounds was also analysed. The influence of food lipids migration to the frying medium on the composition of this latter was evidenced.

1. Introduction

Frying is a culinary process in which both oil and food are modified. The chemical and physical changes provoked in the food result in the acquisition of desirable attributes. The fatty medium also undergoes very complex chemical and physical changes, and the formation of toxic compounds with important repercussions on health is also possible. This culinary process is in worldwide used and due to its complexity, many of its aspects remain unknown and require further research.

The study of the modifications of oils, either heated at frying temperature in absence of food, or used in frying experiments, has been accomplished by methodologies which determine either physical or chemical parameters, such as Iodine Value, conjugated diene values, polar compounds percentage, peroxide and anisidine values or concentration of dimmers, polymers of triglycerides as well as of oxidised triglycerides, (Andrikopoulos, Kalogeropoulos, Falirea, & Barbagianni, 2002; Dobarganes & Márquez-Ruiz, 2007; Kalogianni, Karapantsios, & Miller, 2011; Sánchez-Gimeno, Negueruela, Benito, Vercet, & Oria, 2008). It should be pointed out that from some of the above mentioned parameters it is not easy to extract information about the chemical changes occurring in the friyng medium. Furthermore, the influence of the composition of the food being fried on the chemical changes in the frying medium has been the subject of only a few studies.

This paper deals with the latter subject. To this aim, a study of the evolution of the composition of the frying medium throughout three series of frying experiments on three foods is carried out. This is compared with the evolution of the composition of the original oil submitted to frying temperature in the same fryer but in the absence of food.

In both cases, ^{1}H NMR spectroscopy is applied as in previous studies (Guillén & Uriarte, 2011, 2012a,b,c). The foods selected for the study differ not only in lipid content but also in lipid nature.

This work may provide new information about the effect of the frying process on changes in the composition of the frying medium in comparison with its simple heating; furthermore, this study may also help to clarify the influence of food components on the evolution of the composition of the frying medium by the possible

* Corresponding author. Tel.: +34 945 013081; fax: +34 945 013014.
E-mail address: mariadolores.guillen@ehu.es (M.D. Guillén).

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occurrence of the reactions between components of both systems (medium and food), or by potential migration of the lipidic food components to the frying medium.

2. Materials and methods

2.1. Oil and food samples

The oil used in this study was extra virgin olive oil, acquired in a local supermarket; its composition given in molar percentage of the several kinds of acyl groups (linolenic, Ln, 0.8%; linoleic, L, 6.5%; oleic, O, 80.8%; and saturated, S, 11.9%) was determined from its ^{1}H NMR spectrum as in previous studies (Guillén & Uriarte, 2012a).

One of the foods submitted to frying is frozen commercial dough of Spanish doughnut whose average estimated composition is 29.6% water, 8.0% proteins, 60.8% carbohydrates, and 0.8% lipids, these lipids being made up of 4.0% Ln, 55.0% L, 15.5% O, and 21.5% S. The other food involved in the study is pork adipose tissue, with an approximate composition of 18.0% water, 4.7% proteins, and 76.7% lipids, these latter constituted by 1.7% Ln, 10.2% L, 46.8% O, and 41.3% S. The third food involved is farmed salmon fillets (*Salmo salar*) whose approximate composition is 55.5% water, 17.6% proteins, and 26.2% lipids, these latter formed of 16.0%, omega-3 (ω-3) groups, 10.9% L, 55.9% O or monounsaturated (MU), and 16.8% S. All of them were acquired in local supermarkets. The composition of the lipids of the pork adipose tissue as well as of the farmed salmon fillets, involved in this study, were determined by ^{1}H NMR as in previous studies (Guillén & Uriarte, 2012a; Vidal, Manzanos, Goicoechea, & Guillén, 2012), after extraction using ultrasounds and carbon disulphide as solvent. It should also be noticed that the omega-3 groups of these salmon lipids contain 4.0 ± 0.0% of docosahexaenoic (DHA) acyl groups and 4.7 ± 0.3% of eicosapentaenoic (EPA) acyl groups.

2.2. Experiment of heating at frying temperature of the extra virgin olive oil

For comparative purposes, before carrying out the deep-frying experiments, the extra virgin olive oil was submitted to the same heating conditions but without food. To this aim, 4000 cm^3 of extra virgin olive oil was submitted at 190 °C in an industrial fryer (Franke ECO4, 230 V, 10 A, 2.3 kW) for periods of 8 h/day, for 4 days (the total heating time was 32 h and 30 min); the oil was stored at room temperature between the heating episodes. The dimensions of the stainless steel tank of the fryer were 15 cm wide × 30 cm long × 17 cm high. During heating no oil was replenished. Oil samples were periodically taken and, when necessary, refrigerated until their study in order to avoid or hinder the continuation of the degradation process. This heating experiment was carried out in duplicate before the deep-frying experiments with each food. This extra virgin olive oil submitted to heating at frying temperature was named EVO.

2.3. Deep-frying experiments

Three series of deep-frying experiments, one with each kind of food (Spanish doughnut, pork adipose tissue, and farmed salmon fillets), were carried out. The same initial amount of extra virgin olive oil as described above was used for each series of deep-frying experiments, as was the same industrial fryer and heating conditions. In each series of deep-frying experiments, the oil was heated for 32 h and 30 min (8 h/day for 4 days); in this time 14 frying experiments were carried out. The first frying experiment in each series was done just when the oil reached 190 °C, and the subsequent frying experiments after regular intervals of 2.5 h. 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. Samples of oil of the three series of frying experiments were taken before and after each frying experiment. Each series of frying experiments was carried out in duplicated. The frying media involved in the deep-frying of dough of Spanish doughnut, pork adipose tissue and salmon fillets were named DEVO, PEVO and SEVO respectively.

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

The evolution of the composition of the frying media was monitored by ^{1}H nuclear magnetic resonance. To this aim, the ^{1}H nuclear magnetic resonance spectra of EVO, DEVO, PEVO and SEVO throughout the several experiments (heating and frying experiments), were registered in a Bruker Avance 400 spectrometer operating at 400 MHz. All operating conditions were as in previous studies (Guillén & Uriarte, 2012a).

The ^{1}H NMR spectra of the original oil and of the oil (EVO) and frying media (DEVO, PEVO and SEVO) after 32.5 h of heating or fourteen frying experiments respectively are shown in Fig. 1. Table 1 shows the assignment of the main signals of these spectra; the assignment of some of the signals was made as in previous studies (Guillén & Ruiz, 2003a,b, 2005a,b,c; Guillén & Uriarte, 2012a; Sopelana, Arizabaleta, Ibargoitia, & Guillén, 2013; Vidal et al., 2012) and that of other signals has been made in this paper for the first time. In this study triolein, triestearin, trilinolein and trilinolenin as well as oleic and linoleic acids and some primary and secondary alcohols as well as aldehydes of different types and certain 1,2-diglycerides, and 1,3-diglycerides, were used as standard compounds for both the assignment of certain signals of the spectra and for quantitative purposes.

2.5. Determination of the Iodine Value

The determination of the Iodine Value (IV) was made from ^{1}H NMR data by using a previously developed approach which proved that Iodine Value (Guillén & Ruiz, 2003b) is related to the percentage of olefinic protons (OP%) by the equation

$$IV = 10.54 + 13.39\ OP\%. \quad (1)$$

The percentage of olefinic protons (OP%) in the oil can be directly determined from the area of signal **R** in Fig. 1.

2.6. Determination of the percentage in weight of polar compounds

This parameter was determined throughout the heating or frying experiments by using a Testo 265 instrument. The measurements are based on the dielectric constant of the oil and are directly transformed by the instrument into percentage in weight of polar compounds (PC%).

2.7. Statistic and kinetic studies

The statistical package IMB SPSS Statistics (Version 19) was used to find equations that fit molar percentages of the several kinds of acyl groups of the oil or frying media and heating time.