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Monitoring by ^{1}H nuclear magnetic resonance of the changes in the composition of virgin linseed oil heated at frying temperature. Comparison with the evolution of other edible oils

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ABSTRACT

Linseed oil was heated at frying temperature in an industrial fryer for 20 h. The evolution of its composition was monitored by ^{1}H Nuclear magnetic resonance. The composition parameters determined simultaneously were: the molar percentage of the different acyl groups, the Iodine Value, the concentration of the total aldehydes as well as of the different kinds of aldehydes; in addition, the percentage in weight of Polar Compounds was also determined at different heating times. When heating this oil the molar percentage of linolenic groups diminishes at an important rate while that of linoleic or diunsaturated groups increases, as does that of saturated plus modified groups, that of oleic or monounsaturated groups remaining unchanged. The main aldehydes formed were (*E,E*)-2,4-alkadienals together with *n*-alkanals and (*E*)-2-alkenals. This oil reached the safety limit of 25% in weight of Polar Compounds very early with a very small degradation level of acyl groups and a very low content of aldehydes. The changes undergone by this oil were compared with those of sunflower oil and of extra virgin olive oil submitted to the same degradative conditions.

1. Introduction

The performance of diet lipids at high temperatures is a subject of great interest as heat changes their composition, forming other new compounds. The nature and properties of these latter should be established in order to ascertain their safety and thus ensure consumer health. At low or intermediate (70 °C) temperature and in the presence of air, lipids degrade following the classical scheme of formation of primary or intermediate oxidation compounds which evolve to give secondary oxidation compounds. Under these oxidative conditions it has been observed that the rate of the process is directly associated to the unsaturation degree of the lipids. It has been proved that the higher the unsaturation of the oil, the higher the rate of degradation. So, the total polymerization of extra virgin olive oil submitted to 70 °C with aeration takes place after weeks whereas the total polymerization of linseed oil under the same conditions can occur within hours due to its more rapid oxidation and degradation (Guillén & Ruiz, 2004, 2005a,b,c). The differences in the performance of oils of different compositions under the above mentioned degradative conditions are not only due to the degradation rate but also to the evolution of the process, to the compounds formed and to their safety. In agreement with the above mentioned, linseed oil, one of the richest oils in omega 3 acyl groups, has traditionally been destined to the manufacture of paints given its high level of degradation or polymerization at room temperature. Only in some oriental regions has it been traditionally used for stir-frying (Pan, 1990).

In recent years many papers have reported the healthy properties of omega 3 lipids, especially those of docosahexaenoic, DHA, and eicosapentaenoic, EPA acyl groups particularly associated with cardiovascular benefits (Saravanan, Davidson, Schmidt, & Calder, 2010; Serini, Fasano, Piccioni, Cittadini, & Calviello, 2011); as these latter acyl groups cannot be synthesized by the human organism endogenously, the supplementation of manufactured foods with these and other omega 3 lipids has proliferated in the food industry. Omega 3 lipids used to enrich foods include α-linolenic acyl groups; this supplementation has been carried out on the basis that this acyl group can be elongated endogeneously to form DHA and EPA; however, this possibility has recently become

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controversial (Burdge & Calder, 2006). In short, nowadays there are discrepancies between the beneficial (Barceló-Coblijna & Murphy, 2009; Bassett, Rodriguez-Leyva, & Pierce, 2009; Serini et al., 2011) and the harmful (Burdge and Calder, 2006; Duda et al., 2009; Serini et al., 2011) effects of α-linolenic groups on health and also in relation to its capacity to elongate endogeneously in an effective way. Nevertheless, the enrichment of foods with this acyl group has been increasing and linseed oil is considered an interesting option for this purpose.

One additional problem which has not received much attention is the above mentioned tendency of this kind of lipid to degrade; this fact is of great importance because this degradation may form toxic compounds which can seriously affect the safety of these foods. Given the above, this paper deals with the performance of linseed oil at high temperature, with the changes in its composition detectable by ^{1}H NMR spectroscopy and a comparison with the changes undergone by sunflower oil and extra virgin olive under the same conditions (Guillén & Uriarte, 2012a; Guillén and Uriarte, submitted for publication). This study is of interest not only because, to the best of our knowledge, there are no previous studies on the performance of this kind of oil at such high temperature but also because it can also provide valuable information about the degradation at these high temperatures of the α-linolenic acyl groups also present in small proportions both in other edible oils and in foods enriched with this acyl group whose performance at high temperatures has not been studied before.

2. Materials and methods

2.1. Oil sample and thermodegradation

The oil subject of study was organic virgin linseed oil obtained by cold pressing, acquired in a local supermarket. Its original composition expressed in percentage of acyl groups was determined from ^{1}H NMR data as in previous studies (Guillén & Ruiz, 2003a,b; Guillén & Uriarte, 2009), the percentage of linolenic groups (Ln) being 50.37 ± 0.50%, of linoleic groups (L) 17.85 ± 0.03%, of oleic groups (O) 22.56 ± 0.37%, and of saturated groups (S) 9.20 ± 0.19%.

Four litres of oil were heated in an industrial fryer (Franke ECO4, 230V, 10A, 2.3 kW), at 190 °C, for 20 h, in periods of 8 h/day. The dimensions of the stainless steel tank of the fryer were 15 cm wide × 30 cm long × 17 cm high, the oil-air surface was 450 cm^2 and the initial height of the oil in the tank around 8.9 cm. Throughout the heating process no amount of oil was replenished and the cover was kept closed. Its temperature was periodically tested by a calibrated thermometer. The oil was maintained at room temperature between the heating episodes. Oil samples were taken periodically (every 2 h) and, when necessary, refrigerated until their study in order to avoid or hinder the continuation of the degradation process. The experiment was carried out in duplicate.

2.2. Monitoring of the degradation process by ^{1}H nuclear magnetic resonance spectroscopy

The evolution of the composition of virgin linseed oil was monitored by ^{1}H nuclear magnetic resonance. To this aim, the ^{1}H nuclear magnetic resonance spectra of both the original virgin linseed oil and of the oil after its submission to 190 °C, for different periods of time, under the above mentioned conditions, 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 after to be submitted to different heating times. In this way, the acquisition parameters used were: spectral width 5000 Hz, relaxation delay 3 s, number of scans 64, acquisition time 3.744 s, and pulse width 90°, with a total acquisition time of 12 min 54 s. The experiment was carried out at 25 °C.

Compounds, such as 4-hydroxy-(*E*)-2-nonenal, 4-hydroxy-(*E*)-2-hexenal, acquired from Cayman Chemical (Ann Arbor, MI, USA), and heptanal, octanal, (*E*)-2-heptenal, (*E*)-2-octenal, (*E*,*E*)-2,4-heptadienal, (*E*,*E*)-2,4-nonadienal and (*E*,*E*)-2,4-decadienal, acquired from Sigma Aldrich (St. Louis, MO, USA), were used as standard compounds for identification purposes. Likewise triolein, trilinolein and trilinolenin were acquired from Sigma Aldrich (St. Louis, MO, USA) for quantitative purposes.

All figures of ^{1}H NMR spectra or of expanded ^{1}H NMR spectra regions were plotted at a fixed value of absolute intensity for comparative purposes. The area of the aldehydic proton signals, generated as a consequence of the acyl groups degradation, was determined assigning the unity to the area of the chloroform protons signal (7.28 ppm), which has the same concentration in all ^{1}H NMR experiments as in previous studies (Guillén & Goicoechea, 2007). From these areas, the molar concentrations of these groups of compounds were determined, taking the non-deuterated chloroform as standard compound. All these determinations are possible because the area of the ^{1}H NMR signal is proportional to the number of protons which generates the corresponding signal.

Each sample was analyzed in duplicate or in triplicate and data shown are average values. The ^{1}H NMR spectra of the original oil are shown in Fig. 1. The assignment of the main signals was made as in previous studies (Guillén & Ruiz, 2003a,b) and is given in Table 1.

2.3. Determination of the Iodine Value

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

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

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

2.4. Determination of the percentage in weight of Polar Compounds

This parameter was determined throughout the heating time by the Testo 265 instrument. Testo measurements are based on the dielectric constant of the oil and are directly transformed by the instrument into percentage in weight of Polar Compounds. It measures the dielectric value of the oil by immersion in hot oil and provides the % in weight of Polar Compounds together with the temperature. Accuracy values are: ±2.0% PC (+40 to +190 °C) and ±1.5 °C.

2.5. Statistic and kinetic studies

To find equations that fit the molar percentage of the various kinds of acyl groups in the oil (linolenic, Ln, linoleic, or diunsaturated, L (or DU), oleic or monounsaturated, MU, and saturated plus modified acyl groups (S + M)) and heating time the statistical package Statgraphics Centurion XV was used. Likewise, equations that fit the latter cited parameter and aldehydes concentration