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Addition of Gamma-tocopherol Rich Extract: Impact on Sunflower Oil Degradation Process at Frying Temperatures

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INTRODUCTION

It is well known that during frying, oils degrade and give rise to potentially toxic compounds that could migrate to fried food and thus be absorbed through the diet (1-2). In order to preserve oil quality and safety, compounds showing antioxidant capacity are frequently added, such as tocopherols. Nevertheless, most studies investigating their effect are conducted at room temperature or under accelerated storage conditions, which may not accurately reflect their performance at high temperatures, due to the complexity of the frying process. Furthermore, studies carried out under frying temperatures often employ classical methodologies; they offer limited information on oil degradation level, which may lead to misleading conclusions on antioxidant evaluation. In this context, Proton Nuclear Magnetic Resonance spectroscopy (¹H NMR) has been successfully employed to study food lipids as a whole, not only to characterize them, but also to analyze their oxidation processes under different conditions.

OBJECTIVE

To analyze the impact of adding **0,5** and **3 % of a gamma tocopherol-rich natural extract** on sunflower oil degradation at frying temperatures (170 °C) by investigating potential differences on: the shelf life of frying oil (understood as the time it takes to reach the legal limit of 25 % Polar Compounds (PC)), the degradation of linoleic acyl groups, the generation of compounds derived from oxidation and hydrolysis, and the increase of oil viscosity.

MATERIALS AND METHODS

- Samples: This study was conducted using refined sunflower oil (SO) and a commercial natural extract rich in gamma-tocopherol, extracted from soybean oil. Two types of enriched oil samples were prepared by adding the extract to the control oil (SO) at 0.5 % (SO+05Ext) and 3 % (SO+3Ext) (w.w).
- Heating conditions: Three liters of each type of oil (SO, SO+05Ext, SO+3Ext) were heated in different proffesional fryers in the absence of food at 170 ± 5 °C for 6 hours per day, with the lid removed and until reaching the legal limit of 25 % PC. During heating no additional oil was added and samples were taken in duplicate every 6 hours and stored at -80 °C for subsequent analysis in the following days.
- Percentage of Polar Compounds (PC): This parameter was determined in duplicate every hour during the different heating processes by using a Testo 270 instrument, whose measurements are based on the dielectric constant of the oil, which is directly proportional to the weight percentage of PC present in it.
- Study by Proton Nuclear Magnetic Resonance ('IH NMR): Spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz. The experimental procedure and the assignment of the signals was made as in previous studies (3).
- Viscosity: This physical parameter was measured at room temperature by using a Visco Star Plus+L viscosimeter.

RESULTS AND DISCUSSION

1. EVOLUTION OF % PC AND DEGRADATION OF LINOLEIC ACYL GROUPS



Figure 1. Evolution along the heating experiment of (a) percentage of Polar Compounds (PC) and (b) of the molar percentage of linoleic acyl groups together with the equations of the lines of best fit in control ($S0 \rightarrow$) and enriched oils ($S0+05Ext \rightarrow$ and $S0+3Ext \rightarrow$).

2. GENERATION OF COMPOUNDS RELATED TO OXIDATION

Regarding monoketo-octadecadienoates, both Z,E and E,E isomers were detected at similar concentrations. As can be seen in **Figure 2**, no differences on their evolution were observed among SO and SO+05Ext, whereas at the highest enrichment level these oxidation products were generated at the highest concentrations (compare SO+3Ext with SO).

As **Figure 3** shows, aldehydes of the same nature were generated in both non-enriched and enriched oils. In all the samples, *E*,*E*-2,4-alkadienals, *E*-2-alkenals and alkanals were those detected at the highest concentrations, although slight quantitative differences were found among samples. In the presence of tocopherol-rich extract, there was a reduced formation of *E*,*E*-2,4-alkadienals, *E*-2-alkenals, alkanals and 4-oxoalkanals, being especially noticeable at the highest enrichment level (S0+3Ext). By contrast, in the presence of the extract the generation of *E*,*Z*-2,4-alkadienals seemed to be favored (compare S0+3Ext with S0 and S0+05Ext). **Figure 1a** shows that in all the samples % PC gradually increased as heating time progressed, as expected. The legal limit for safe use (25 %) was reached **before** in enriched samples (126 h for SO+3Ext and 138 h for SO+05Ext) than in the control oil (144 h), indicating that the higher the degree of enrichment with the gammatocopherol rich extract, the **shortest** the time to reach the legal limit of 25 % PC.

As easily observed in **Figure 1b**, linoleic groups degrade the **fastest** in the oil enriched at the highest level, being the rate of degradation in SO+3Ext of -0.1014 whereas in SO it is of -0.0736. In the case of SO+05Ext, a slightly higher degradation (-0.0862) than in SO was also noticed. These results would confirm that adding the assayed tocopherol rich-extract would not increase frying oil stability, but decrease it. These results are in agreement with the differences commented before on the evolution of % PC in these samples.



Figure 2. Evolution of the concentration of Z,E and E,E -monoketo-octadecadienoates in control (SO ------) and enriched oils (SO+OSExt ---- and SO+3Ext -----) along the heating experiment, expressed as millimol/mol acyl group (mmol/mol AG).



h h h h Figure 3. Evolution of the concentration of *E*,*E*-2,4-alkadienals, *E*-2-alkenals, alkanals, *E*,*Z*-2,4-alkadienaks and 4-oxoalkanals in control (50-) and enriched oils (50+05Ext and 50+3Ext) along the heating experiment, expressed as mmol/molAG

3. GENERATION OF COMPOUNDS RELATED TO HYDROLYSIS REACTIONS



Figure 4. Evolution of the concentration of 1,2-diglycerides (1,2-DG) in control (SO_) and enriched oils (SO+05Ext_) and SO+3Ext_) along the heating experiment, expressed as millimol/mol acyl group (mmol/mol AG).

As for hydrolysis products, no differences among the three types of oils were observed up to 80 h of heating. Afterwards, 1,2-diglycerides were generated at higher concentration in SO+3Ext, confirming the higher degradation of sunflower oil when adding the tocopherol-rich extract at 3 %(see **Figure 4**).

4. INCREASE OF OIL VISCOSITY

As an indirect way of studying the generation of polymers, the viscosity of the frying oil was monitored over the heating process (see Figure 5). In line with that previously observed regarding % PC and linoleic chains degradation, the enrichment of sunflower oil with the tocopherol extract markedly enhanced the increase of viscosity.



- CONCLUSIONS
- □ The assayed gamma tocopherol-rich extract was unable to protect sunflower oil towards degradation at frying temperatures at any concentration. Indeed, adding this natural extract to the oil decreased its stability, providing it with a lower shelf life (understood as the time it takes to reach the legal limit of 25 % PC) and enhancing linoleic groups degradation and polymer formation over heating time.
- Although little, certain differences in the profile of oxidation products generated were observed, indicating that adding this extract altered to some extent the kinetics and/or pathways of reactions.
- From the nutritional point of view, special attention should be paid to the higher increase of oil viscosity when adding the extract, as more frying oil would be absorbed by
 the food and consumed.

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