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Effect of Rosemary Extract on Sunflower Oil Oxidation Process under different Conditions. A Proton Nuclear Magnetic Resonance (^{1}H NMR) Spectroscopy Study

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INTRODUCTION

Rosemary extract (RE) is a commercially available natural extract that can be added to food products as antioxidant. This activity is attributed mainly to its phenolic diterpenes carnosic acid and carnosol, and has widely been studied under different conditions, either accelerated storage or at frying temperatures, in the presence or absence of food. Most studies described an antioxidant effect of RE using classical methodologies, such as Peroxide Value or Conjugated Dienes, but these provide limited information on the nature of the compounds being generated. By contrast, ^{1}H NMR spectroscopy has shown to be a great tool to address this kind of study, because it provides information not only about the degradation rate of the oil components, but also about the nature and evolution of the products being formed during the process.

Considering all the above, this study aimed to investigate the effect of the addition of RE to sunflower oil oxidation process. RE was added in a proportion that the final concentration of carnosol plus carnosic acid was 0,02 % and the samples were submitted to frying conditions in the absence of food (170 ºC) and to accelerated storage conditions (70 ºC).

MATERIALS AND METHODS

RE was added at 0,02% to sunflower oil. Enriched and non-enriched samples were submitted to different conditions:

- **Accelerated storage at 70 ºC with aeration**: 10 g of oil were placed in Petri dishes in an convection oven until polymerization.
- **Frying temperature at 170 ºC in the absence of food**: 3 L of oil were heated in professional fryers until the oil reached the legal limit of 25 % of total polar compounds (measured by a Testo 270 instrument).

Aliquots of each type of sample were periodically analyzed by **^{1}H NMR** (*1*).

OBJECTIVE

To study by means of ^{1}H NMR the effect of the addition of RE at 0,02% on sunflower oil degradation process under accelerated storage and frying temperature.

RESULTS AND DISCUSSION

Results under frying temperature at 170 ºC:

Under frying conditions, RE did not exert any protective effect on the oil. Thus, the degradation rate of **LINOLEIC ACYL GROUP** was **very similar** in **both enriched and non-enriched** samples (see Figure 1). It must be noted that both kinds of oils reached at the same time the legal limit of 25 % of total **polar** compounds (138 h).

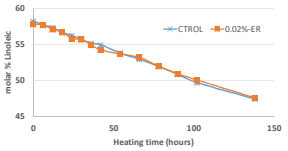

Figure 1. Evolution of the molar percentage of linoleic acyl group under frying temperature in control oil (non-enriched) and in ER-0.02% enriched oil.

Although incipient signals due to **hydroperoxides supporting diene conjugated systems** were observed, the concentration of these **PRIMARY OXIDATION COMPOUNDS** was very low, probably due to the instability of these compounds at high temperatures.

In agreement with that observed on linoleic acyl group, hardly any differences were detected in the generation of **SECONDARY OXIDATION PRODUCTS** between the enriched and non-enriched samples.

The only **difference** observed between the **enriched** and **non-enriched** samples was the concentration reached by **alkanals** and, mainly, ***E,E*-2,4-alkadienals**, which was slightly lower along the process when ER was added at 0,02% (see **Figure 2**).

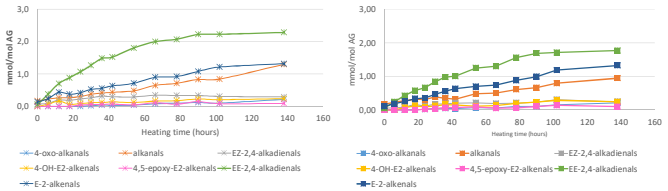

Figure 2. Evolution of the concentration of certain aldehydes generated under frying temperature (170 ºC) in **a)** control oil (non-enriched); **b)** ER-0.02% enriched oil.

Results under accelerated storage at 70 ºC:

In contrast to that observed when oils were submitted to 170 ºC, under accelerated storage at 70 ºC **the addition of ER at 0,02%** exerted a **great protective effect** on the degradation of **LINOLEIC ACYL GROUP** (see **Figure 3**), in such a way that in control oil linoleic groups were sharply degraded from day 4 onwards and in ER enriched oil from day 12 onwards.

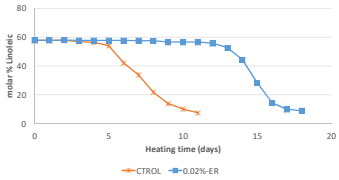

Figure 3. Evolution of the molar percentage of linoleic acyl group under accelerated storage conditions in control oil (non-enriched) and in ER-0.02% enriched oil.

The formation of **HYDROPEROXIDES SUPPORTING DIENE CONJUGATED SYSTEMS** was significantly delayed in the sample enriched with 0,02% of ER (see **Figure 4**), in line with that observed for linoleic groups degradation. These primary oxidation products reached a slightly lower concentration in the enriched oil, mainly regarding to *E,E*-hydroperoxy-dienes.

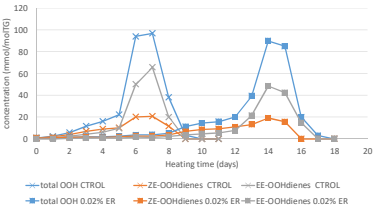

Figure 4. Evolution of the concentration of hydroperoxides supporting diene conjugate systems in control oil (non-enriched) and in ER-0.02% enriched oil submitted to 70 ºC.

Since hydroperoxides degrade to give rise to **SECONDARY OXIDATION COMPOUNDS**, the enrichment of sunflower oil with 0,02% of ER also delayed the formation of these later in a proportional way. In control oil they were detected from day 5 onwards, and in enriched oil from day 13 onwards, in agreement with that observed on linoleic groups degradation (see Figure 3). As an example, Figure 5a and 5b show the evolution of the concentration of non-oxygenated and oxygenated aldehydes, respectively, in both enriched and non enriched samples.

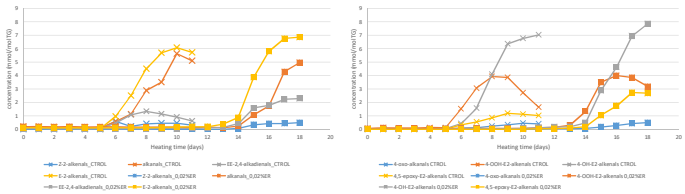

Figure 5. Evolution of the concentration of different kinds of aldehydes in control oil (non-enriched) and in ER-0.02% enriched oil submitted to 70 ºC: **a)** non-oxygenated aldehydes; **b)** oxygenated aldehydes.

CONCLUSIONS

- Under **frying** conditions in the absence of food (170 ºC), RE added to sunflower oil at 0,02 % **did not** exert any protective effect on the oil.
- On the contrary, under accelerated **storage** conditions (70 ºC), RE showed an **antioxidant** effect, delaying both the degradation of oil components (linoleic) and the formation of primary (hydroperoxides) and secondary (aldehydes) oxidation products.
- Thus, it has been evidenced that the **performance of antioxidant** compounds **can vary under different degradative conditions**. Therefore, to asses properly the effectiveness of antioxidants it is of great importance use the **conditions as close as possible** to the conditions under which protection against oxidation is required, and also to use **specific methodologies** (like ^{1}H NMR) able not only to follow the degradation of oil components but also to identify which products are generated and/or inhibited by the presence of antioxidants.

REFERENCES

(*1*) Guillén, M.D. and Ruiz-Aracama, A. (2004). Formation of hydroperoxy- and hydroxyalkenals during thermal oxidative degradation of sesame oil monitored by proton NMR. Eur. J. Lipid Sci. Technol., 106: 680-687.

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