19th Euro Fed Lipid Congress and Expo
17–20 September 2023 Poznań · Poland

eman ta zabal zazu
Universidad del País Vasco
Euskal Herriko Unibertsitatea

PROCAYSEAL RESEARCH GROUP
Food Processing, Quality and Safety
www.ehu.eus/procayseal

INFLUENCE OF MATRIX COMPOSITION ON THE EFFECT OF HYDROXYTYROSOL ACETATE ON OIL OXIDATION

Weinbinder, D.D., Manzanos, M.J., Ibargoitia M.L., Sopelana, P.*
Food Technology, Faculty of Pharmacy, Lascaray Research Centre, University of the Basque Country (UPV/EHU).
Paseo de la Universidad, 7, 01006 Vitoria-Gasteiz, Spain. *E-mail: patricia.sopelana@ehu.eus

INTRODUCTION

The oxidative stability of oils rich in polyunsaturated acyl groups is a crucial aspect that influences their quality, since oxidation can lead to nutrient losses, development of off-flavours and generation of toxic compounds. Consequently, much research has been carried out on the effect of numerous compounds and extracts with potential antioxidant capacity on edible oil stability (1). In this context, hydroxytyrosol acetate has been shown to be effective in reducing oil oxidation under accelerated storage conditions (2). Notwithstanding, more information is needed in order to be able to select the most appropriate antioxidants for different types of oils, since their composition could influence the observed effect.

OBJECTIVE

To **study** the **influence of matrix composition** on the **effect of hydroxytyrosol acetate** on the **oxidation process** of **three** different **types of edible oils**, all of them very **rich in polyunsaturated acyl groups**.

MATERIALS AND METHODS

SAMPLES: **Refined sunflower oil (RSO)**, **virgin linseed oil (VLO)** and **refined microalgae oil** containing 5000 ppm of an extract rich in tocopherols (E-306) **(RMO)**, and **these same oils enriched with hydroxytyrosol acetate (OHTyrAc)** in a proportion of 0.1% by weight: **RSO + OHTyrAc**, **VLO + OHTyrAc** and **RMO + OHTyrAc**.

OXIDATION: The oils (6.5 g in glass Petri plates of 5 cm diameter) were submitted to an accelerated storage process at 70 °C in an oven with aeration. For each oil, aliquots were taken periodically from the same plate until total polymerization.

STUDY OF THE SAMPLES: The samples were studied before and at different times of the accelerated storage process by ^{1}H Nuclear Magnetic Resonance (^{1}H NMR).

RESULTS AND DISCUSSION

1. SOME COMPOSITIONAL ASPECTS OF THE STUDIED OILS

As **Table 1** shows, the three types of oils differ both in their acyl group composition and in some minor components with attributed antioxidant ability, such as tocopherols. Differences in acyl groups are reflected in the unsaturation degree of the oils ($R_{S/U}$), **RMO** being the most unsaturated one and **RSO** the least. While in **RSO** α-tocopherol (α-T), the main tocol present in this type of oil (3), was not in high enough concentration to be detected by ^{1}H NMR, in **RMO** an elevated level of γ-T was found.

Table 1. Mean values of molar percentage of the main polyunsaturated (PU) group present in each oil, degree of unsaturation ($R_{S/U}$), the most abundant tocopherol (T) in each oil and its concentration, expressed in millimoles per mole of triglyceride (mmol/mol TG).

	RSO	VLO	RMO
Main PU group / molar %	Linoleic / 60.1	Linolenic / 47.2	ω-3* / 43.5
$R_{S/U}$ (ratio of saturated to unsaturated protons)	9.9	6.4	2.5
Main tocopherol / mmol/mol TG	α-T / nd	γ-T / 1.10	γ-T / 9.85

*: mainly DHA; nd: not detected

2. EVOLUTION OF THE CONCENTRATION OF THE MAIN POLYUNSATURATED ACYL GROUPS AND OF OHTyrAc

- A reduction in the degradation rate of the samples enriched with OHTyrAc is observed (see **Figure 1**), which leads to an enlargement in the time needed to reach oil total polymerization. The extent of this effect is considerably pronounced for **RSO** sample, in accordance with previous studies (2), less marked for **VLO** and very slight for **RMO**. Consequently, after 9 days, the greatest decrease in the loss of the main polyunsaturated acyl group is found in **RSO + OHTyrAc**, the least unsaturated oil (see **Table 1**), whereas differences are hardly noticed in **RMO**, the most unsaturated one.
- The concentration of OHTyrAc decreases with time (see **Figure 2**), although the rate of this drop varies depending on the oil. Thus, OHTyrAc takes a little longer to degrade in **RSO**, where the antioxidant effect of this compound seems to be the most intense (see **Figure 1**), than in **VLO**. Instead, in **RMO** oil OHTyrAc diminishes much more rapidly. Considering previous results obtained with mixtures of OHTyrAc and α-T (4), it could be thought that, similarly to α-T, γ-T, present in high concentration in **RMO** (see **Table 1**), might have interacted with OHTyrAc, counteracting to some extent its antioxidant potential in this oil.

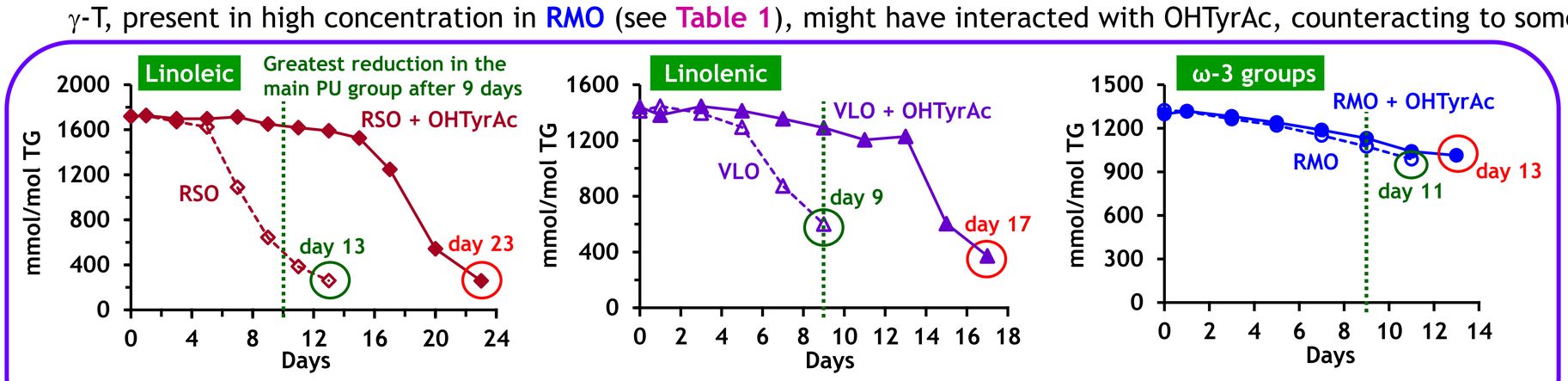

Figure 1. Evolution of the concentration, expressed in millimoles per mole of triglyceride (mmol/mol TG), of linoleic, linolenic and ω-3 acyl groups in the corresponding oils over the storage time.

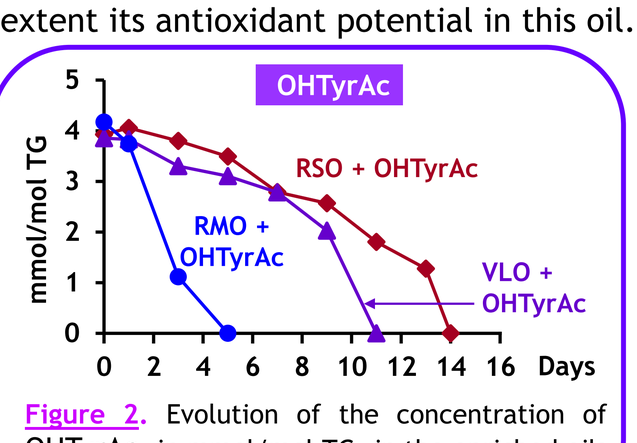

Figure 2. Evolution of the concentration of OHTyrAc, in mmol/mol TG, in the enriched oils over the storage time.

3. GENERATION OF OXIDATION PRODUCTS

- The effect of the OHTyrAc enrichment on the formation of oxidation derivatives is in accordance with that observed on the evolution of the main polyunsaturated acyl group in each oil. Thus, considerable reductions in the generation rate of hydroperoxides (data not shown) were noticed especially in **RSO**, but also in **VLO**. However, in **RMO** the addition of OHTyrAc hardly prevents the formation of oxidation compounds.
- The delay in primary oxidation compound generation results in a later appearance of those secondary ones like aldehydes. This deserves special interest, since the addition of OHTyrAc greatly reduces the formation of some potentially toxic oxygenated α,β-unsaturated ones in **RSO** and **VLO** during a considerable period of time (see **Figure 3**).

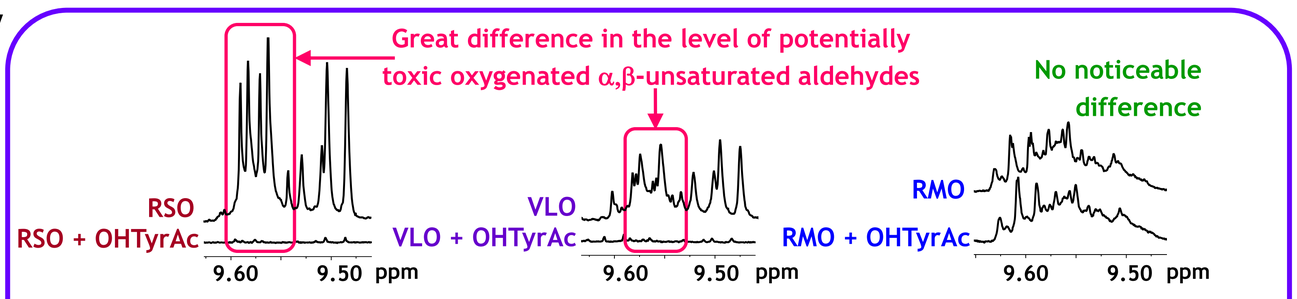

Figure 3. ^{1}H NMR signals attributable to certain classes of unsaturated aldehydes in the spectra of the samples after 9 days under accelerated storage conditions.

CONCLUSIONS

- The **effect of OHTyrAc on oil oxidation rate** is **influenced by the matrix composition**, it being very pronounced for sunflower, and to a somewhat lesser extent, for linseed oil, but very weak for microalgae oil. These findings suggest that the higher the unsaturation degree of the oils, the weaker the antioxidant effect of OHTyrAc. However, the high concentration of γ-T in the microalgae oil might also have contributed to the scarce effect of OHTyrAc observed in this oil compared with the other ones.
- **Further studies** are needed in order to **know** the possible **interactions between OHTyrAc and other minor components** that can be present in edible oils, either naturally or because of an addition, in order to elucidate how these could affect its behaviour.

REFERENCES

1. Mishra SK, Belur PD, Iyyaswami R (2021) *Int J Food Sci Technol*, 56, 1.
2. Caño-Ochoa SD, Ruiz-Aracama A, Guillén MD (2022) *Antioxidants*, 11, 722.
3. Alberdi-Cedeño J, Ibargoitia ML, Cristillo G, Sopelana P, Guillén MD (2017) *Food Chem*, 221, 1135.
4. Caño-Ochoa SD, Ruiz-Aracama A, Guillén MD (2022) *Antioxidants*, 11, 1156.

ACKNOWLEDGEMENTS: This work has been supported by the Basque Government (EJ-GV IT1490-22). D.D. Weinbinder thanks for a predoctoral contract supported by the European Union-Next Generation EU through the Investigo Programme.