The double-edged sword of halophyte plants in the quality of vegetable oils

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INTRODUCTION

Natural alternatives to synthetic antioxidants have been sought by the oil food industry to enhance the oxidative stability of oils. Halophyte plants such as *Salicornia ramosissima* (SR), have been added directly to vegetable oils with such purpose [1]. This fortification can be related to positive and negative effects in the oil quality, **Figure 1**. As a tentative to reduce the potential release of salt from the plant, during the oil fortification, and the further production of MCPDs contaminants, an ethanolic extract of dried SR was added to enhance the oil oxidative stability upon frying.

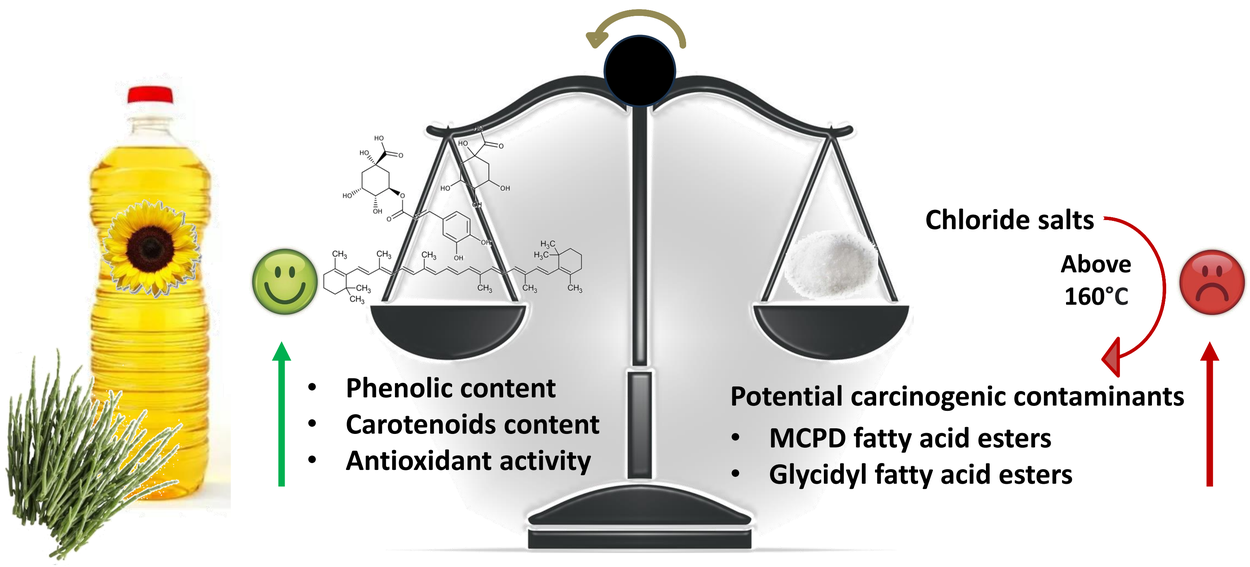

Figure 1. Adding *Salicornia ramosissima* (SR) to the oil may have **positive** and **negative** impact in the oil quality [2]

OBJECTIVE

- Characterize the **phenolic content** and the **volatile composition** of sunflower oil before and after fortification.
- Determine **MCPDs and glycidyl fatty acid esters** in the control sunflower oil and in the fortified sunflower oil.

METHODS

i) Fortification of sunflower oil with an extract of SR:
The dried *Salicornia,* milled to 0.8 mm was extracted in ethanol (2g:100mL) [3]. After fortification for 24h, the ethanol was evaporated. The fortified and the control oils, were submitted to frying temperatures of 160 – 170 °C, following two cycles of 8h. Experiments were performed in duplicate.

ii) Total Phenolic Content (TPC): Assessed by HPLC-DAD-ED (Vanquish Thermo) as described elsewhere [3].

iii) Volatile composition: By SPME-GC-MS/MS (solid phase microextraction coupled to the gas chromatograph using mass spectrometry detection). The identification of the compounds was based on spectra libraries (NIST 21, 27, 107, 147 and Wiley 229). For the relative compound's quantification, the compound's area was normalized by the total chromatogram's area. The differences in volatile compounds' abundance were emphasized by partial least square discriminant analysis (PLS-DA).

iii) MCPDs and Glycidyl fatty acid esters: Following alkaline transesterification and measurement by GC-MS/MS in accordance with the ISO 18363-4:2021.

RESULTS AND DISCUSSION

i) SR extract and the phenolic composition of fortified sunflower oil

SR ethanolic extract with a TPC of **1500 ± 250** µg gallic acid equivalent, GAE/ g of dried SR was added to the oil (**6%** of SR).
After incorporation of the phenolic extract, the fortified oil had a phenolic content of **13.6** µg GAE/g oil, which represented **15%** of the total added phenolic content.

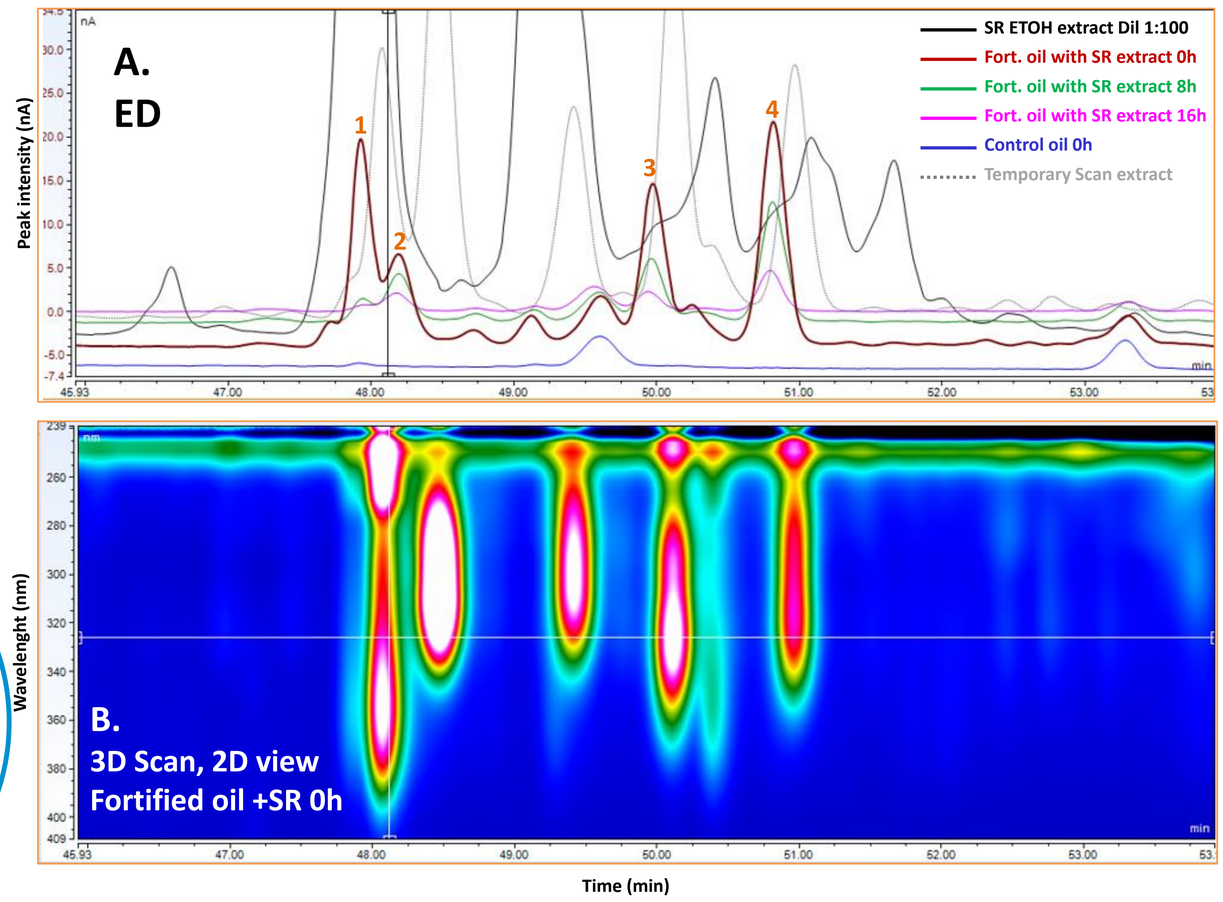

Figure 2. A. ED chromatogram showing some electrochemical active compounds, **1** to **4**. **B.** 3D Scan in a 2D view showing the maximum absorbance wavelength of diverse compounds in the extract of the fortified sunflower oil before frying (0h).

Most of the **phenolic compounds** (tentatively identified by mass spectrometry elsewhere [3] as **1.** Isorhamentin-rutinoside derivative; **2.** Rhamnetin-hexosyl pentoside; **3.** and **4.** p-coumaric acid derivatives) with **signal in the Electrochemical detector** (ED), in the **fortified oil extract**, at 0h, 8h and 16h, **derived from the SR** extract, were **flavonols** or **hydroxycinnamic acids**, based on the maximum absorbance wavelength and retention time. Although the relative abundance of these **electrochemically active compounds reduced upon frying, their presence even after 16h at frying temperatures may contribute to the oxidative stability of the oils**.

ii) Volatile composition of sunflower oil without and with SR

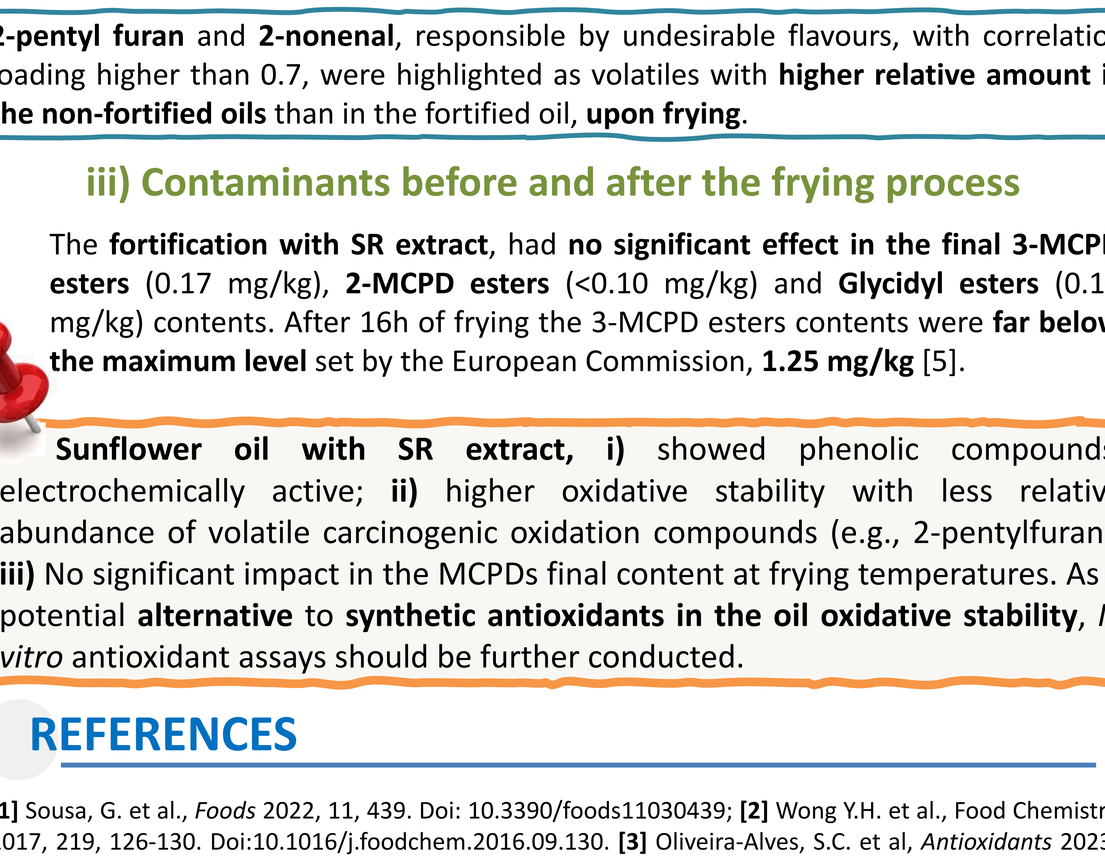

Figure 3. Score plot obtained by **PLS-DA**, showing the correlation between the defined **groups** (oil samples, analysed in duplicate (1 and 2), without fortification, **NO FORT**, and oil samples with *Salicornia* extract fortification, **FORT**, after 8h and 16h of frying process), and the predictors (volatile compounds' normalized area).

2-pentyl furan and **2-nonenal**, responsible by undesirable flavours, with correlation loading higher than 0.7, were highlighted as volatiles with **higher relative amount in the non-fortified oils** than in the fortified oil, **upon frying**.

iii) Contaminants before and after the frying process

The **fortification with SR extract**, had **no significant effect in the final 3-MCPD esters** (0.17 mg/kg), **2-MCPD esters** (<0.10 mg/kg) and **Glycidyl esters** (0.16 mg/kg) contents. After 16h of frying the 3-MCPD esters contents were **far below the maximum level** set by the European Commission, **1.25 mg/kg** [5].

Sunflower oil with SR extract, i) showed phenolic compounds, electrochemically active; **ii)** higher oxidative stability with less relative abundance of volatile carcinogenic oxidation compounds (e.g., 2-pentylfuran); **iii)** No significant impact in the MCPDs final content at frying temperatures. As a potential **alternative** to **synthetic antioxidants in the oil oxidative stability**, *In vitro* antioxidant assays should be further conducted.

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