

Article

Stabilization of Sunflower Oil with Biologically Active Compounds from Berries

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Abstract: Sunflower oil (*Helianthus annuus*) contains a rich concentration of polyunsaturated fatty acids, which are susceptible to rapid oxidative processes. The aim of this study was to evaluate the stabilizing effect of lipophilic extracts from two types of berries, sea buckthorn and rose hips, on sunflower oil. This research included the analysis of sunflower oil oxidation products and mechanisms, including the determination of chemical changes occurring in the lipid oxidation process via LC-MS/MS using electrospray ionization in negative and positive mode. Pentanal, hexanal, heptanal, octanal, and nonanal were identified as key compounds formed during oxidation. The individual profiles of the carotenoids from sea buckthorn berries were determined using RP-HPLC. The influence of the carotenoid extraction parameters ascertained from the berries on the oxidative stability of sunflower oil was analyzed. The dynamics of the accumulation of the primary and secondary products of lipid oxidation and the variation of the carotenoid pigment content in the lipophilic extracts of sea buckthorn and rose hips during storage demonstrated good stability at 4 °C in the absence of light for 12 months. The experimental results were applied to mathematical modeling using fuzzy sets and mutual information analysis, which allowed for the prediction of the oxidation of sunflower oil.

Keywords: sunflower oil; carotenoids; sea buckthorn; rose hips; lipid oxidation; oxidative stability



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1. Introduction

A permanent concern in the modern food industry is to ensure an optimal shelf life of food products. The main factor that leads to food spoilage is oxidation [1,2]. Oxidation is a chemical process involving the modification of fatty acids, amino acids, and vitamins, which, in turn, affects the organoleptic and nutritional characteristics of food [3,4].

The oxidation of lipids in food is a complex process that is influenced by various factors, such as the chemical structure of the food; the food's physical condition; the quantity and quality of substances that act as antioxidants in food; and the processing, packaging, and storage conditions of the food. Lipids are an easily alterable fraction of food, so their storage conditions largely depend on their nature and concentration. The consequences of this process, which are precipitated by the degradation of some easily oxidizable constituents of the lipid fraction in food, can include the appearance of a rancid odor, color changes, and, in some cases, changes in food texture, which negatively influence the sensory parameters of food [5]. The nutritional value of foods subjected to oxidative degradation of their lipid fraction can also be affected to a considerable extent. However,

the most important risk is the ingestion of lipid oxidation products because they present enormous toxicological risks and, in the case of long-term use, can lead to the appearance of degenerative pathologies such as arteriosclerosis, cancer, etc.

After soybean oil, sunflower oil (*Helianthus annuus*) ranks second in the world in terms of the most-produced edible oils and is rightly considered to number among the preeminent vegetable oils for the human diet due to its nutritional value [6]. Sunflower oil contains a high concentration of polyunsaturated fatty acids (especially oleic and linoleic acids) that contribute to lowering cholesterol and reducing the risk of heart disease. However, polyunsaturated fatty acids are the site of rapid oxidative processes, especially in the presence of oxygen and light. Plant sterols or phytosterols are compounds with proven health benefits. Their richest natural sources are vegetable oils. In crude sunflower vegetable oil, phospholipids represent 0.8–1.2% of the total lipid fraction [7]. Unsaturated fatty acids esterified in phospholipids are major targets for oxidation. The hydrogen atoms on the methylene groups adjacent to the double bonds (allylic hydrogen atoms) present low C-H bond energies, and those located on the methylene between two double bonds (hydrogen bis-allylic) have even lower C-H bond energies. This fact allows them to be easily abstracted by reactive radical species, leading to the formation of phospholipid radical species with the radical centered on the allylic carbon atom. Refinement and deodorization processes considerably decrease the content of phospholipids (0.1–0.2%). This increases the stability of the oils upon oxidation but decreases their biological value [8].

In biological materials, lipids are protected from oxidation by the presence of antioxidants and cell membranes, which reduce the access of oxidants to easily oxidizable fractions [3]. In food, reducing the impact of lipid oxidation can only be ensured by the use of appropriate packaging and by the presence of antioxidants, which block the propagation or decomposition of hydroperoxides. Food products usually contain antioxidants of a synthetic origin (propyl gallate—E-311 or octyl gallate—E-312; butylhydroxyanisole (BHA)—E-320; etc.), but their effect on human health is debatable. One of the current strategies used in the food industry with the aim of inhibiting the lipid oxidation process is the use of natural antioxidants, which are compounds that increase the shelf life of food products following the oxidation process [9]. Lipophilic extracts from vegetable powders of berries, which are rich in biologically active compounds, are of particular interest [10–12].

Tocopherols are the most important antioxidants present in edible oil. Sunflower oil contains a high concentration of tocopherols (648.9 ppm). The refinement process, especially deodorization, reduces tocopherol content [13–15]. Carotenoids are a group of tetraterpenoids that are formed from isoprenoid units and have conjugated double bonds. In the co-presence of chlorophylls, β -carotene reduces the oxidation of edible oil by inhibiting $^1\text{O}_2$ [16,17]. Sea buckthorn (*Hippophae rhamnoides* L.) is a valuable plant due to its medicinal and nutritional potential, as it is a good source of bioactive compounds such as vitamins (C, E, and K; riboflavin; and folic acid), carotenoids (α -, β -, and δ -carotene; lycopene), tocopherols, phytosterols, organic acids (malic acid, oxalic acid, and citric acid), polyunsaturated fatty acids, and some essential amino acids [18–20]. Rose hip berries (*Rosa canina* L.) are rich in polyphenols, carotenoids, triterpenic acids, essential fatty acids, galactolipids, folates, vitamins C and E, minerals (Ca, Mg, K, S, Si, Se, Mn, and Fe), etc. [21]. It has been reported that rose hips can be used not only for direct consumption but also for the extraction of bioactive compounds (BC) [22].

The aim of this study was to assess the stabilizing effect of lipophilic extracts from berries—sea buckthorn and rose hips on sunflower oil. Firstly, we determined the optimal conditions for obtaining the lipophilic extracts from the berries. Secondly, an analysis of the products and mechanisms of sunflower oil oxidation was conducted. This included determining the chemical changes that occur in the process of a forced lipid oxidation analysis of the evolution of the stability parameters of the stabilized oils over a period of 12 months, mathematically modeling the oxidation processes, and determining the influencing factors.

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