

PLANT OILS AS ALTERNATIVE SOLVENTS FOR VALORIZATION OF FRUIT BY-PRODUCTS

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Abstract

Extraction of lipophilic phytochemicals from plant matrices with edible oils could result in ready-to-use extracts whose valuable physical, chemical and biological properties determine their suitability for inclusion in final product's composition. For the aims of the current study, almond and grape seed oils were chosen as green solvents for the extraction of antioxidants from by-products of *Physalis peruviana* fruits after juicing. Achieving specific amounts of β -carotene (β -Car.) in the oils was a result of the application of two different approaches: (i) addition of the individual substance and (ii) extraction from the plant material. Their photo-oxidative stability was studied and compared. Addition of individual carotene in a range 0.002–0.05% could significantly improve the oxidation stability of oils. Ultrasonic extraction of dried residues of *P. peruviana* fruits resulted in the enrichment of almond and grape oil with carotenoids, including β -Car., by about 0.004%, but without any observed reduction in the oxidation rate(s).

Key words: green solvents, vegetable oils, carotenoids, antioxidants, lipid oxidation

Introduction. The idea of investigating the ability of vegetable oils to replace organic solvents for the extraction of bio-molecules from agriculture and food

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processing side streams combines more than one principle of Green Chemistry: a zero-waste integration, safer solvents, application of novel extraction techniques requiring less energy consumption. In addition to their advantageous characteristics (non-toxic, non-volatile, non-irritating, non-polar, not expensive), these oils also have the advantage that they could be directly incorporated into food and cosmetic products [1]. Applying edible oils as alternative solvents for the extraction of lipid soluble phytochemicals from plant materials could result in ready-to-use extracts whose valuable physical, chemical and/or biological properties determine their suitability for inclusion in the composition of a final product [2].

Lipids are important for the intake and absorption of carotenoids (Car.) in the diet [3]. Besides their role in the growth and development of the human body and in the maintenance of normal physiological functions, Car. also attract attention as pigments. The vast diversity of carotenoid structures makes it difficult to classify plant foods in terms of the content of these physiologically significant molecules [4]. Some natural sources are distinguished by a higher total carotenoid content than others, which in turn have a richer carotenoid spectrum. *P. peruviana* L., a member of Solanaceae family, known also as goldenberry and cape gooseberry, can be considered a promising source for juices, nectars and puree production [5]. The by-products obtained after processing are regarded as valuable sources of amino acids, organic acids, minerals, vitamins and Car. [6,7]. The pomace contains 19.3% oil, 17.8% protein, 3.10% ash, 28.7% crude fibre and 24.5% carbohydrates [6]. Among the secondary metabolites, 22 carotenoid compounds from *P. peruviana* were identified, all-trans- β -Car. was the major carotenoid contributing 76.8% to the total carotenoid, followed by 9-cis- β -Car. (3.6%) and all-trans- α -cryptoxanthin, contributing around 3.4% [6]. According to PETKOVA et al. [7] the total phenolic content was higher in the extracts obtained from the pulp compared to those from the goldenberries.

The aim of the present work was to obtain functional oils by extracting lipid-soluble antioxidants from a goldenberry by-product based on the application of almond and grape seed oils, popular vegetable oils, as green solvents. Furthermore, an additional goal was to study their photo-oxidative stability on the basis of the comparison not only with both unfortified oils (as control samples) but also with oils fortified by the addition of individual β -Car. at concentration(s), consistent and close to that achieved after extraction.

Materials and methods. Plant material, solvents and reagents. The berries (*P. peruviana* L.) were purchased from one of the largest chain stores in Bulgaria, and the origin of the fruits is Colombia (year 2024). Grape seed and almond oils were purchased from a Bulgarian producer and used without additional purification. All organic solvents are of analytical and/or HPLC grade. β -carotene and α -, β -, γ - and δ -tocopherol standards (TOHs) for HPLC analysis were purchased from Sigma Aldrich (St. Louis, MO, USA).

Processing *P. peruviana* L. fruits. The ripe fruits were separated from their calyxes, washed and pulped according to MOKHTAR et al. [8]. The husks and small pieces of pulp were separated from the seeds by flotation and then filtered and dried at 45 °C for 24 h.

Extraction procedure. For organic solvent (hexane) extraction as well as oil-based extraction, the parameters were similar to those used by TSOGTOO et al. [9]: 0.5 g of dried and ground plant material and 5 g of vegetable oil (ratio 1:10) were introduced in 10 ml glass bottle (covered with foil). Samples were sonicated (30 min at room temperature) in water bath JULABO SW22 (JULABO GmbH, Seelbach, Germany). After filtration oil samples were stored at the dark at 4 °C for further analysis and oxidation stability assessment.

HPLC analysis. The content of TOHs and Car. in studied oils were determined according to the method published previously by us [10].

A Shimadzu system, consisting of a DGV-20A 5R degassing unit, LC-30AD pump, SIL-30AC autosampler, CTO-20AC column oven, RF-20AXS fluorescence detector, SPD-M30A DAD diode array detector and CBM-20A controlling unit was employed. Separation was carried out on a LUNA SILICA (2) column (5 µm, 250 × 4.6 mm; Phenomenex, USA) at 25 °C with hexane:dioxane (95:5, v/v) as the mobile phase at 1 ml/min. The injection volume was 10 µl. TOHs were detected fluorometrically (Ex 292 nm, Em 325 nm), and Car. were monitored at wavelength 470 nm using a DAD detector. Peak areas of the individual compounds were compared to those of analytical standards. Concentrations are given as mg/100 g of dry weight.

Determination of oxidative stability of fortified and unfortified grape seed and almond oils. In addition to the oils obtained after ultrasonic extraction of plant tissues according to the procedure described above, oil samples containing different concentration of β -Car. were also prepared. By adding aliquots of acetone solutions of β -Car. to almond and grape seed oils, final concentrations in the range 0.02–0.93 mM (0.001–0.05%) were obtained. All samples, fortified and non-fortified oils (control samples) were poured in 1 mm layers into Petri dishes and stored at room temperature (22 ± 2 °C) and in daylight. A kinetic regime (oxygen-sufficient conditions) was ensured storing the samples in this way. The lipid oxidation process was monitored by measuring peroxide value PV over time [11] and kinetic curves were plotted based on the mean PV value of three independent experiments.

Statistics. Statistical differences between the two sample groups were evaluated using the Student's *t*-test. The results were considered statistically significant at $p < 0.05$. All analyses were performed using Statistica 14.1.0.4 (StatSoft Inc., Tulsa, OK, UAS).

Results and discussion. Table 1 presents the amounts of target lipid-soluble compounds extracted by a conventional method using an organic solvent (hexane). The total tocopherol content achieved with hexane from the by-products

T a b l e 1

Naturally occurring antioxidants in pomace of *P. peruviana* fruits (without seeds)

Compound	mg / 100 g _{dw}
total TOHs	23.72 ± 0.16
α -TOH	1.43 ± 0.02
β -TOH	2.87 ± 0.31
γ -TOH	18.66 ± 0.16
δ -TOH	0.76 ± 0.16
total carotenoids (Car.)	103.09 ± 1.90
β -Car.	55.90 ± 1.43

of *P. peruviana* fruits was 23.72 mg per 100 g dry weight with γ -TOH as a major component the amount of which is 13- and 6.5-fold higher than that of α - and β -TOH, respectively (Table 1).

For oil-based extractions, the conditions were the same as those used for the aforementioned organic solvent extraction. Grape seed oil and almond oil were chosen, both used for special culinary applications, in food additives but mainly as ingredients in cosmetic preparations. Among the many vegetable oils for skin care, almond oil shows excellent nourishing and smoothing properties. It is also rich in monounsaturated oleic acid (18:1). Given the fact that carotenoids are light-sensitive and unstable, our choice was directed towards oils with a relatively low proportion of polyunsaturated fatty acids in the composition. On the other hand, grape seeds are by-product of the wine industry but are considered a valuable source of phytochemicals. The oil from the seeds is rich in linoleic (C18:2) and oleic (C18:1) acids but contains also tannins which together with the tocopherols are responsible for its relatively high oxidative stability.

Figure 1 presents concentrations of TOHs and Car. in grapeseed and almond oil before and after sonication in absence of plant matrices, as well as after ultrasonic extraction in presence of dried plant material of *P. peruviana* L. in a ratio 1:10, the orange and red bar-graphs, respectively.

Ultrasonic treatment of the oils does not have a significant effect on the content of TOHs or at least no significant differences are observed immediately after its application. From the obtained results, it is evident that among TOHs, statistically detectable differences were observed only for the content of γ -TOH in both studied oils after the extraction (Fig. 1). Obviously, the increase in γ -TOH is due to release from the plant matrix into the oil during extraction.

Photo-oxidation of oils (Fig. 2) proceeds by different mechanisms from those typical of spontaneous autooxidation, i.e. under no light. In the first case, the key role plays the singlet oxygen $^1\text{O}_2$, while in the second case, the decomposition of lipid hydroperoxides to free radicals attacking lipid molecules and interacting with

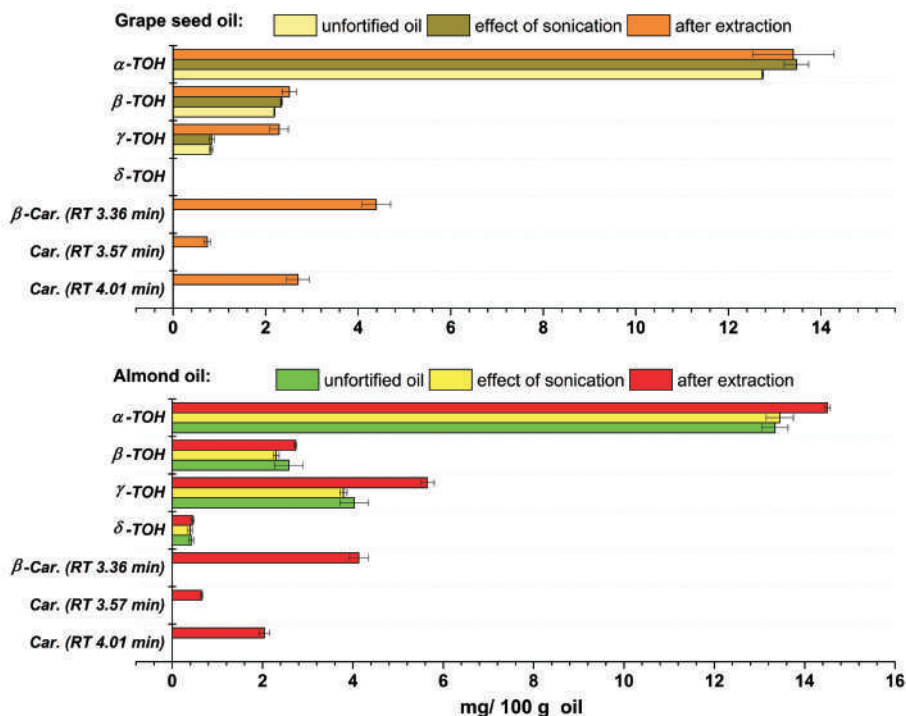


Fig. 1. Tocopherol and carotenoid content of grape seed and almond oils before and after sonication (30 min) in absence and in presence (ratio 1:10) of plant material (deseeded *P. peruviana* pomace)

atmospheric oxygen is crucial. Therefore, many antioxidants that are effective under autoxidation conditions do not show oxidative activity during photo-oxidation and vice versa.

β -Car. is proved to be an effective quencher of $^1\text{O}_2$ [12] and thus its inclusion in foods containing unsaturated oils could improve their stability and shelf live. The degree of unsaturation of the lipid matrices affects the oxidative stability of oils, but does not affect the solubility of β -Car. The latter increases with decreasing the chain length of the fatty acids involved in the lipid molecules' structure(s).

Achieving specific amounts of β -Car. in the studied vegetable oils, within the framework of the present study, is a result of applying two different approaches:

- addition of the individual substance (commercial product) with a certain purity;
- extraction from plant material, dried pomace of *P. peruviana* fruits (without seeds).

To our knowledge, this is the first time that comparisons of the photo-oxidative stability of oils obtained by the two methods, mentioned above, have

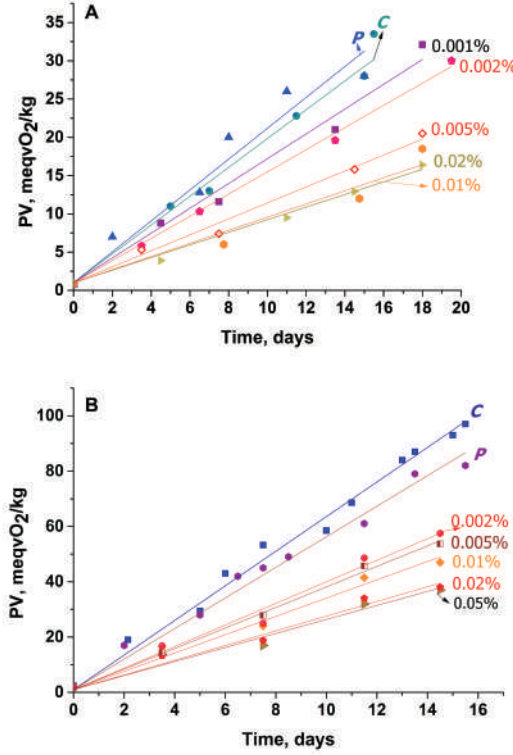


Fig. 2. Kinetics of lipid hydroperoxides accumulation during photo-oxidation (under natural light) of almond (A) and grape seed oil (B) before (control sample C) and after enrichment with β -Car. (0.001–0.05%) or extraction of Car., including β -Car., from deseeded *P. peruviana* pomace (P)

been made. From the results obtained (Fig. 2), it is evident that β -Car. suppresses oxidation, reducing its rate in a concentration-dependent manner, which is in accordance with results published by other authors [13] in different model systems.

The following order of decreasing oxidation rate's values in the presence of β -Car. in the concentration range 0.02–0.93 mM (0.001–0.05%) for the almond oil was obtained (the values in parentheses for the rates were measured in moles per second M/s):

$$\beta\text{-Car.}^{0.001} (0.91 \cdot 10^{-8}) \geq \beta\text{-Car.}^{0.002} (0.88 \cdot 10^{-8}) > \beta\text{-Car.}^{0.005} (0.61 \cdot 10^{-8}) > \\ > \beta\text{-Car.}^{0.01} (0.53 \cdot 10^{-8}) \approx \beta\text{-Car.}^{0.02} (0.52 \cdot 10^{-8}) > \beta\text{-Car.}^{0.05} (0.46 \cdot 10^{-8}).$$

And by analogy for the grapeseed oil:

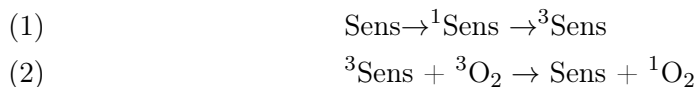
$$\beta\text{-Car.}^{0.001} (2.32 \cdot 10^{-8}) > \beta\text{-Car.}^{0.002} (2.21 \cdot 10^{-8}) > \beta\text{-Car.}^{0.005} (2.11 \cdot 10^{-8}) > \\ > \beta\text{-Car.}^{0.01} (1.86 \cdot 10^{-8}) \approx \beta\text{-Car.}^{0.02} (1.49 \cdot 10^{-8}) > \beta\text{-Car.}^{0.05} (1.42 \cdot 10^{-8}).$$

The measured photo-oxidation rates of control samples, i.e., non-fortified almond and grape seed oils, were $1.04 \cdot 10^{-8}$ M/s and $3.56 \cdot 10^{-8}$ M/s, respectively. These rates decreased after addition of β -Car., as can be seen from Fig. 2. This effect increased with increasing its concentration β -Car.^{0.001}– β -Car.^{0.05}.

Grape seed oil oxidizes 2 to 3 times faster than almond oil, at the same carotene concentrations, because the former is much more unsaturated. In the presence of 0.93 mM (0.05%) β -Car., the oxidation rate of both oils was reduced by half.

After extraction of the dried plant material, the content of β -Car. is 4.13 mg and 4.39 mg per 100 g almond and grape seed oil (Fig. 1), i.e. 0.0041% and 0.0044%, respectively. The calculated molarities are 0.077 mM and 0.082 mM ($\approx$ 0.08 mM for both oils). Although the achieved amounts of β -Car. are close to 0.09 mM (0.005%), the oxidation rates of oils after extraction were not reduced at all and were even close to these of the control (non-fortified) oils.

Probably, along with the lipid-soluble antioxidants, TOHs, tocotrienols and Car., other compounds can be extracted too, some of which sensitizers. The sensitizers, such as chlorophylls, absorb light energy and go into their first excited state (reaction 1), followed by intersystem crossing to a metastable triplet state:



Then, an interaction with the ground state triplet oxygen is possible (reaction 2), resulting in ${}^1\text{O}_2$ formation [12]. There are ways to remove sensitizers such as chlorophylls according to protocols using organic solvents [14]. However, this is still a challenge in the field of Green chemistry.

Conclusions. The potential of using vegetable oils as food-grade solvents for extraction of carotenoids, tocopherols and other lipid-soluble phytochemicals was verified. Fortification of almond and grape seed oil with antioxidants could be achieved by the application of two different approaches: (i) addition of the individual substances and (ii) extraction from plant matrices (by-products of *P. peruviana* fruits after juicing). To our knowledge, this is the first time that comparisons of the photo-oxidative stability of oils fortified by both methods, have been made. The experiments carried out within the frame of the current study showed that oil stability could be improved significantly after addition of individual β -Car. in a range 0.002–0.05%. The achieved amounts of β -Car. after extraction with the oils fall within this concentration range but without any observed reduction in the oxidation rate(s). Probably, along with the lipid-soluble antioxidants, other compounds were extracted too, some of which sensitizers, the removal of which would be necessary for some applications in practice.

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