

Oxidative stability, physico-chemical and sensory properties of mayonnaise enriched with carotenoids from sea buckthorn pomace during refrigerated storage

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Summary

Sea buckthorn (*Hippophae rhamnoides*) pomace, a by-product from the juice industry, is a promising source of nutritional and bioactive compounds that could be used as an ingredient of functional food. In this research, sea buckthorn by-products were used as a source of carotenoids and other lipophilic bioactive compounds to be incorporated in mayonnaise through direct extraction in the oil used in the manufacture of mayonnaise. Effects of sunflower oil enrichment after extraction of 50 g·l⁻¹ and 100 g·l⁻¹ dried sea buckthorn pomace (DSB) on oxidative stability and sensory properties of mayonnaise during a 28 days storage at 4 °C were investigated and compared with addition of 1 g·l⁻¹ butylated hydroxytoluene (BHT) and control. Titratable acidity, Hunter colour values, peroxide values (*PV*), thiobarbituric acid reactive substances (*TBARS*) and sensory attributes were determined in mayonnaise samples immediately after preparation and after 14 and 28 days of storage. Samples enriched with carotenoids from 50 g·l⁻¹ DSB had significantly ($p < 0.05$) lower *PV* and *TBARS* values as compared to control samples and recorded the highest scores for all sensory attributes as well as overall acceptability throughout the storage period. However, extraction from 100 g·l⁻¹ DSB negatively affected the physico-chemical and sensory characteristics of mayonnaise during storage.

Keywords

sea buckthorn pomace; oil; extraction; mayonnaise; colour; lipid oxidation

Mayonnaise, one of the most popular and widely used sauces in the world today, is an oil-in-water emulsion containing 70–80 % fat, produced by emulsifying vegetable oil with other components like eggs and mustard [1–3]. It is highly appreciated for its special flavour and creamy mouthfeel. However, mayonnaise is susceptible to lipid oxidation due to the high oil content and the nature of the raw materials, namely, the high content of unsaturated fatty acids in vegetable oils [4, 5]. Lipid oxidation is generally initiated at the interface between the oil and aqueous phases and progresses in the oil phase during storage [6, 7]. This process is associated with generation of lipid free radicals and results in the formation of off-flavour, toxic components and discoloration, which affect the organoleptic and nutritional properties as well as the storage stability of mayonnaise [2, 5, 8].

A common strategy to prevent or delay the oxidative damage is the addition of synthetic antioxidants such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) or ethylene-

diaminetetraacetic acid (EDTA), but they are associated with possible detrimental effects on human health. Therefore, there has been a growing interest in replacing synthetic antioxidants with those obtained from natural resources [2, 9]. Moreover, enrichment of mayonnaise with functional ingredients, such as natural antioxidants, could lead to an innovative and healthier food product [10].

Most of the studies conducted so far focused on the enrichment of oil-in-water (O/W) emulsions with natural antioxidants from plant materials rich in phenolic compounds, such as extracts from berries [11], green tea [12], olives [13], olive leaves [10], grape seed [14], buckwheat hull [9], purple corn [2] or ginger powder [15]. However, carotenoids are also excellent direct free radical scavengers and important natural sources of orange, yellow and red oil soluble food colouring [16]. As a result, extracts from carotenoid-rich fruits and vegetables could be a good option to enrich the traditional recipe of mayonnaise in order to prevent the oxidative lipid damage and to

intensify the typical pale yellow colour of mayonnaise originating from the egg yolk.

Sea buckthorn berries are currently of great interest thanks to their nutraceutical properties and high antioxidant contents. Juice processing from sea buckthorn berries leads to a residual pomace accounting for 20 % of the total fruit weight, consisting of pulp, seed and skin, which is rich in carotenoids, polyphenols, fatty acids and sterols [17–20]. In order to produce high-value natural food additives and supplements, and to reduce the waste, the recovery of bioactive compounds from sea-buckthorn by-products have gained increasing interest in recent years [21]. Direct extraction of lipophilic bioactive compounds, mainly carotenoids, tocopherols, tocotrienols and fatty acids, from sea buckthorn by-products in vegetable oils could be used for the enrichment of these oils in order to improve their quality and functionality as well as to increase the dietary carotenoid intake [22].

The present research focused on utilization of sea buckthorn by-products as a source of carotenoids and other lipophilic bioactive compounds to be incorporated in mayonnaise. Therefore, the purpose of the present study was to evaluate the use, in the manufacture of mayonnaise, of a vegetable oil enriched with bioactive compounds directly extracted from by-products of sea buckthorn processing in order to improve the colour, oxidative stability and sensory quality of mayonnaise during storage.

MATERIALS AND METHODS

Sea buckthorn pomace

Samples of sea buckthorn pomace were collected from Biocat Prod, a commercial producer and processor of sea buckthorn from Gradina (44°31'N, 28°27'E), Constanta county, South-East Romania. These by-products included peels, seeds and residual pulp, resulting from berries after the juice extraction by pressing. As soon as obtained, sea buckthorn by-products were packed in plastic bags and frozen at $-25\text{ }^{\circ}\text{C}$. Subsequently, they were dried in a hot air industrial dryer (Blue Spark Systems, Bucharest, Romania) at $60\text{ }^{\circ}\text{C}$, then ground to a powder, packed in aluminium-coated polyethylene bags and stored in ambient conditions for a maximum of six months.

Materials and chemicals

All ingredients used to prepare the mayonnaise, such as refined sunflower oil, eggs, salt, lemon juice and mustard, were purchased from a local market in Craiova, South-West Romania.

Butylated hydroxytoluene (BHT), thiobarbituric acid, potassium persulfate, trichloroacetic acid, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) and malondialdehyde were obtained from Sigma-Aldrich (St. Louis, Missouri, USA). 2,2'-Azino-bis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS) was obtained from Alfa Aesar (Karlsruhe, Germany). All other chemicals used were of analytical grade and were purchased from Merck (Darmstadt, Germany).

Extraction of dried sea buckthorn pomace in oil

Samples of dried sea buckthorn pomace (DSB) were subjected to maceration at $20\text{ }^{\circ}\text{C}$ in refined sunflower oil (C) at $50\text{ g}\cdot\text{l}^{-1}$ (DSB5) and $100\text{ g}\cdot\text{l}^{-1}$ (DSB10) concentration for ten days. The extractions were followed by filtration through Whatman No. 1 filter paper (Whatman, Maidstone, United Kingdom) and the resulting oils were collected in screw-capped dark plastic containers completely filled with oil and stored at $4\text{ }^{\circ}\text{C}$ for a maximum of two weeks. The commercial sunflower oil was also stored under the same conditions as the extracted oils, to be used as control.

Preparation of mayonnaise

Four different mayonnaise formulations were prepared: MC (control), MBHT (made with sunflower oil with $1\text{ g}\cdot\text{l}^{-1}$ BHT addition), MDSB5 (made with sunflower oil macerated with $50\text{ g}\cdot\text{l}^{-1}$ DSB) and MDSB10 (made with sunflower oil macerated with $100\text{ g}\cdot\text{l}^{-1}$ DSB). Mayonnaise samples were prepared in a glass beaker of 14 cm diameter. The recipe was based on the following formulation (all amounts are stated in percentage, w/w): sunflower oil (84.8 %), egg yolk (10.9 %), mustard (1.7 %) and lemon juice (2.7 %). The preparation was carried out by mixing the egg yolks and mustard together until completely combined and then by adding oil gradually under continuous mixing. Lemon juice was incorporated after all the oil had been added and the mayonnaise emulsion had been formed. Mayonnaise samples were packed in 500 ml disposable plastic containers, wrapped externally with aluminum foil to exclude light, and stored refrigerated at $4\text{ }^{\circ}\text{C}$ for 28 days. The samples were prepared in triplicate (3 batches per formulation type) and each sample was used only once for the measurement.

Acid values (AV), Hunter colour values, peroxide values (PV), thiobarbituric acid reactive substances (TBARS) and sensory attributes were determined in mayonnaise samples immediately after preparation and after 14 and 28 days of storage.

Physico-chemical properties of the oils

PV and *AV* values were measured in control and extracted oils before preparation of mayonnaise samples using the AOAC Official Methods 965.33 and 940.28, respectively [23].

Total carotenoid content

Total carotenoid content of the oils was determined spectrophotometrically as described by SZYDŁOWSKA-CZERNIAK et al. [24]. The oil samples (1 g) were dissolved in 50 ml of *n*-hexane and absorbance at 450 nm was measured against *n*-hexane using a Varian Cary 50 UV spectrophotometer (Varian, Palo Alto, California, USA) in a quartz cell with an optical path of 1 cm. A calibration curve of β -carotene standard solutions in *n*-hexane (0.1–7.0 mg·l⁻¹) was used to determine the carotenoid content of oil samples. The final results were expressed as milligrams of β -carotene per kilogram of oil.

Antioxidant activity

Antioxidant activity of the oils was determined using the ABTS assay according to the procedure described by RE et al. [25]. The ABTS cation radical solution (ABTS^{•+}) was prepared by mixing 5 ml of a 7.0 mmol·l⁻¹ ABTS solution and 88 μ l of a 145 mmol·l⁻¹ potassium persulfate solution. The mixture was incubated in the dark at room temperature for 16 h. The ABTS^{•+} solution was then diluted with 80% ethanol to an absorbance of 0.70 \pm 0.02 at 734 nm. Samples of 120 μ l were mixed with ABTS^{•+} solution (12 ml) and absorbance was recorded after 6 min against ethanol as a blank. The standard curve was constructed using Trolox and the results were expressed in millimoles Trolox per kilogram of oil.

pH measurement

pH values of mayonnaise samples were measured at 20 °C with a Hanna pH meter HI255 equipped with a glass electrode (Hanna Instruments, Padova, Italy) using a 10% dispersion of mayonnaise in distilled water.

Acid value

Free fatty *AV* of mayonnaise samples was determined using the AOAC 940.28 method [23]. The results were expressed as grams of KOH per kilogram of sample.

Peroxide value

PV was determined according to the AOAC 965.33 method [23] on the lipids of the sample. Oils were extracted from mayonnaise as described by PARK et al. [9]. Portions of 30 g

of the mayonnaise were poured into 50 ml polypropylene centrifuge tubes. The samples were frozen at –18 °C for 24 h and thawed for 2 h at room temperature in darkness to break the emulsion. The thawed samples were then centrifuged for 10 min at 7000 \times g. The separated lipid phase was used directly for *PV* analysis. Briefly, 2 g of the oil phase of the mayonnaise was dissolved in 20 ml chloroform:acetic acid (1:2, v/v). Then, 1 g potassium iodide was added and the mixture was mixed by vortex for 1 min. Approximately 20 ml potassium iodide solution 5% and 50 ml distilled water were added and the liberated iodine was titrated with sodium thiosulfate (0.1 mol·l⁻¹) in the presence of 0.5 ml starch solution as indicator. Peroxide value was expressed as milliequivalents of active oxygen per kilogram of sample.

Thiobarbituric acid reactive substances value

TBARS value was determined spectrophotometrically according to the procedure described by WITTE et al. [26] with slight modifications. For extraction, 5 g of the mayonnaise sample were homogenized in a vortex with 12.5 ml of 20% trichloroacetic acid, then transferred to a 25 ml volumetric flask and diluted up to the marked volume with cold distilled water. After filtration, 5 ml of filtrate were mixed with 5 ml of 0.02 mol·l⁻¹ 2-thiobarbituric acid and heated at 100 °C for 35 min. After cooling, the absorbance was recorded at 532 nm with a Varian Cary 50 UV spectrophotometer. The results were calculated from the standard curve of 1,1,3,3-tetraethoxypropane and expressed as milligrams of malondialdehyde per kilogram of sample.

Colour measurement

The colour of oils and mayonnaise samples was evaluated by measuring the *L*^{*} (lightness), *a*^{*} (redness/greenness) and *b*^{*} (yellowness/blueness) values of the CIELAB system using a Thermo Scientific Evolution 600 UV/VIS spectrophotometer (Thermo Fisher Scientific, Waltham, Massachusetts, USA) calibrated against a white standard. The analysis was performed on three samples from each formulation with five readings for each sample.

Sensory evaluation

Mayonnaise samples were evaluated after preparation as well as after 14 and 28 days of refrigerated storage in terms of colour, odour, taste, consistency and overall acceptability. A nine-point hedonic scale was used with 1 = extremely dislike and 9 = extremely like. The sample presentation order was randomized. The panel consisted of 10 members from staff of the Department of

Food Science, University of Craiova (Craiova, Romania). Before each session, the panelists were trained on each attribute, the hedonic scale used and what they need to consider during the evaluation.

Statistical analysis

All experiments were run in triplicate and results were reported as mean \pm standard deviation. In order to assess the effects of formulations and storage time, data were subjected to the analysis of variance (ANOVA) using Statgraphics Centurion XVI software (Statgraphics Technologies, Warrenton, Virginia, USA). Duncan's multiple-range test was used to test for difference between means with the significance defined at $p < 0.05$.

RESULTS AND DISCUSSION

The total carotenoid content of the oil increased approximately 12-fold (to 55.17 mg·kg⁻¹) and 21-fold (to 97.18 mg·kg⁻¹) after extraction of 50 g·l⁻¹ and 100 g·l⁻¹ dried sea buckthorn by-products, respectively. As a result, the extraction of dried sea buckthorn by-products significantly modified the colour parameters of the oils ($p < 0.05$). The L^* values decreased slightly after DSB extraction, indicating a slight darkening of the oils (Tab. 1). The a^* and b^* values increased significantly, meaning increased redness and yellowness, respectively. These changes could be attributed to the extraction of carotenoids, predominantly β -carotene and zeaxanthin, in the oils [22]. The enrichment with carotenoids led to a significant increase in the ABTS antioxidant activity

of the oils (Tab. 1). DSB extraction caused a slight increase in AV and PV of the oils, however, the differences between oil samples were not significant ($p < 0.05$).

Colour is a main sensory characteristic of food products affecting the consumers' purchasing or tasting decision. In general, the typical pale yellow colour of mayonnaise originates from the egg yolk and oil, which may be further influenced by the addition of mustard, additives or some other spices with colouring effects [10]. The production of mayonnaise with oils enriched with carotenoids after extraction from dried sea-buckthorn pomace led to significant colour changes of the mayonnaises, since the oils themselves had a darker orange colour originating from the higher content of carotenoids of 55.17 mg·kg⁻¹ and 97.18 mg·kg⁻¹ for DSB5 and DSB10, respectively, as compared with the control oil (4.56 mg·kg⁻¹; Fig. 1). The colour of the mayonnaise samples enriched with carotenoids from DSB was yellow with increasing intensity depending on the amount of DSB extracted (Fig. 2).

The use of oils enriched with carotenoids after DSB extraction resulted in a decrease in lightness and an increase in redness of mayonnaise as compared with the control and BHT-added samples. ALTUNKAYA et al. [14] reported also that the addition of grape seed extract decreased the lightness of the mayonnaise samples, while increased the redness. Huge differences in a^* and b^* values were found between control samples and mayonnaise made with carotenoid-enriched oil, MDSB10 having the highest a^* and b^* values while MC the lowest. This might be due to the high content of carotenoid pigments of the MDSB5 and MDSB10

Tab. 1. Acid values, peroxide values, total carotenoid content and antioxidant activity of control and experimental oils.

	C	DSB5	DSB10
Total carotenoid content [mg·kg ⁻¹]	4.56 \pm 0.34 ^a	55.17 \pm 2.68 ^b	97.18 \pm 4.55 ^c
Acid value [g·kg ⁻¹]	1.28 \pm 0.06	1.34 \pm 0.08	1.38 \pm 0.10
Peroxide value [meq·kg ⁻¹]	1.60 \pm 0.12	1.72 \pm 0.14	1.86 \pm 0.16
Antioxidant activity [mmol·kg ⁻¹]	3.63 \pm 0.17 ^a	4.26 \pm 0.23 ^b	4.88 \pm 0.22 ^c
L^*	83.52 \pm 1.52	81.71 \pm 2.12	80.75 \pm 0.79
a^*	-0.12 \pm 0.15 ^a	1.81 \pm 1.38 ^b	5.25 \pm 0.64 ^c
b^*	9.21 \pm 0.57 ^a	45.39 \pm 8.68 ^b	69.11 \pm 3.66 ^c

Data are expressed as mean \pm standard deviation. Values with different letters in superscript are significantly different from each other ($p \leq 0.05$) according to Duncan's multiple range test. Total carotenoid content is expressed as milligrams of β -carotene per kilogram of oil. Acid value is expressed as grams of KOH. Peroxide value is expressed as milliequivalents of active oxygen. Antioxidant activity is expressed as millimoles of Trolox.

C – control refined sunflower oil, DSB5 – sunflower oil macerated with 50 g·l⁻¹ DSB, DSB10 – sunflower oil macerated with 100 g·l⁻¹ DSB, L^* – lightness colour coordinate, a^* – redness/greenness colour coordinate, b^* – yellowness/blueness colour coordinate.

samples, which most likely contributed to the behaviour of mayonnaise during storage.

Colour changes in lightness (L^*), redness (a^*) and yellowness (b^*) of mayonnaise samples during 28 days storage at 4 °C are shown in Tab. 2. The lightness and yellowness decreased during storage in all the mayonnaises, while redness slightly increased, as seen in the changes in the L^* , a^* and b^* values. However, results showed that there were insignificant changes in a^* value of both control and carotenoid-enriched mayonnaise samples during 28 days of storage. At the end of storage, the highest L^* values were observed in mayonnaise added with 1 g·l⁻¹ BHT and the lowest a^* values were found in control sample, while the lowest L^* value and the highest a^* and

b^* values were found in the samples made with sunflower oil extracted with 50 g·l⁻¹ DSB. The darkening of mayonnaise samples during storage may be attributed to non-enzymatic browning reactions having as a substrate the carbonyl compounds generated during lipid oxidation, as well as to the brown-coloured oxypolymers produced via polymerization from the lipid oxidation derivatives [27].

The pH and AV of mayonnaise samples recorded during 28 days of storage are given in Tab. 3. pH values of freshly prepared mayonnaise samples ranged between 4.35 and 4.48. During storage, the pH values decreased slightly in all mayonnaise samples with control samples showing the highest pH decrease. At day 28, the pH values of MC,

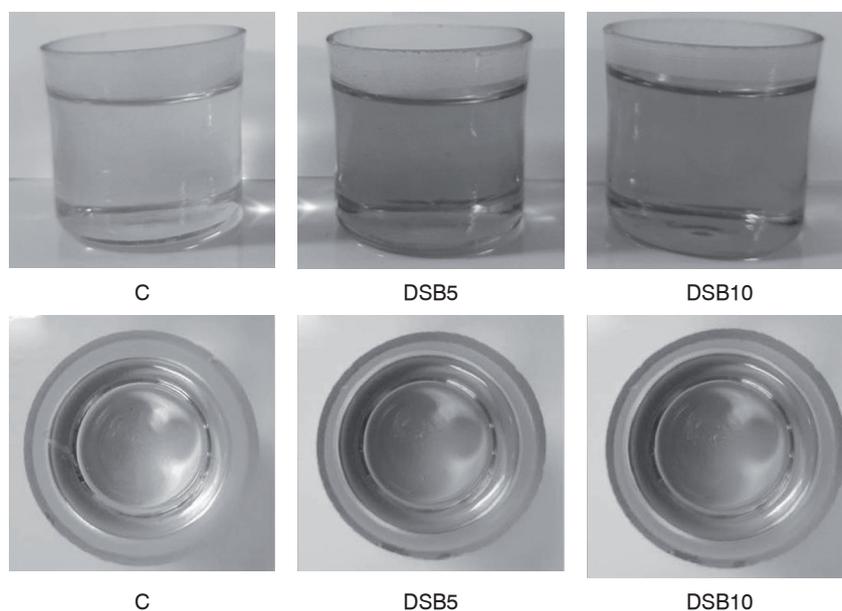


Fig. 1. Control and experimental oil samples.

C – control refined sunflower oil, DSB5 – sunflower oil macerated with 50 g·l⁻¹ dried sea buckthorn pomace, DSB10 – sunflower oil macerated with 100 g·l⁻¹ dried sea buckthorn pomace.

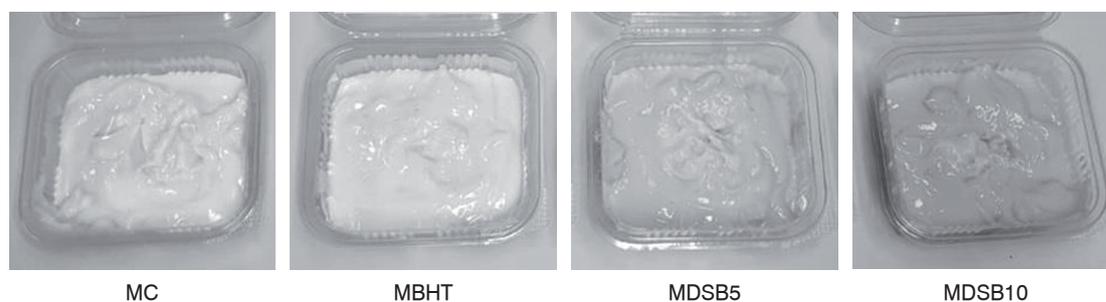


Fig. 2. Control and experimental mayonnaise samples.

MC – control mayonnaise, MBHT – mayonnaise made with 1 g·l⁻¹ butylated hydroxytoluene addition, MDSB5 – mayonnaise made with sunflower oil macerated with 50 g·l⁻¹ dried sea buckthorn pomace, MDSB10 – mayonnaise made with sunflower oil macerated with 100 g·l⁻¹ dried sea buckthorn pomace.

Tab. 2. Effect of storage on Hunter colour values of mayonnaise samples.

Storage time [d]	MC	MBHT	MDSB5	MDSB10
L*				
0	90.83 ± 2.25 ^{bB}	89.99 ± 2.05 ^{abB}	86.67 ± 2.41 ^{abA}	85.95 ± 2.51 ^{aA}
14	88.67 ± 1.82 ^{cB}	87.44 ± 1.88 ^{bcAB}	84.11 ± 1.62 ^{abA}	83.39 ± 1.86 ^{aA}
28	82.22 ± 1.27 ^{abA}	85.83 ± 2.06 ^{bA}	83.64 ± 2.27 ^{abA}	81.48 ± 2.36 ^{aA}
a*				
0	-3.36 ± 0.69 ^{aA}	-3.35 ± 0.61 ^{aA}	-1.61 ± 0.46 ^{bA}	-1.28 ± 0.45 ^{bA}
14	-3.07 ± 0.94 ^{aA}	-3.03 ± 0.90 ^{aA}	-1.54 ± 0.54 ^{abA}	-1.15 ± 0.84 ^{bA}
28	-2.73 ± 0.50 ^{aA}	-2.58 ± 0.77 ^{aA}	-1.36 ± 0.43 ^{bA}	-1.06 ± 0.52 ^{bA}
b*				
0	21.47 ± 0.87 ^{aB}	22.86 ± 2.84 ^{aA}	50.95 ± 3.83 ^{bB}	55.79 ± 2.18 ^{bC}
14	19.51 ± 1.01 ^{aAB}	19.81 ± 2.69 ^{aA}	46.71 ± 2.93 ^{bAB}	48.35 ± 2.59 ^{bB}
28	18.84 ± 1.12 ^{aA}	18.96 ± 1.97 ^{aA}	42.81 ± 2.57 ^{bA}	43.29 ± 2.10 ^{bA}

Data are expressed as mean ± standard deviation. Different lowercase letters in superscript indicate significant difference at $p < 0.05$ level between different formulations, while different uppercase letters in superscript are indicative of the same within each formulation during the storage period.

MC – control mayonnaise, MBHT – mayonnaise made with 1 g·l⁻¹ butylated hydroxytoluene addition, MDSB5 – mayonnaise made with sunflower oil macerated with 50 g·l⁻¹ dried sea buckthorn pomace, MDSB10 – mayonnaise made with sunflower oil macerated with 100 g·l⁻¹ dried sea buckthorn pomace, L* – lightness colour coordinate, a* – redness/greenness colour coordinate, b* – yellowness/blueness colour coordinate.

Tab. 3. Effect of storage on pH, acid values, peroxide values and thiobarbituric acid reactive substances of mayonnaise samples.

Storage time [d]	MC	MBHT	MDSB5	MDSB10
pH				
0	4.44 ± 0.02 ^{bC}	4.38 ± 0.04 ^{aC}	4.35 ± 0.02 ^{aC}	4.48 ± 0.03 ^{bC}
14	4.36 ± 0.03 ^{cB}	4.29 ± 0.02 ^{bB}	4.24 ± 0.03 ^{abB}	4.28 ± 0.02 ^{abB}
28	3.80 ± 0.02 ^{aA}	3.93 ± 0.03 ^{cA}	3.88 ± 0.02 ^{bA}	3.90 ± 0.02 ^{bcA}
Acid value [g·kg⁻¹]				
0	0.87 ± 0.03 ^{aA}	0.87 ± 0.03 ^{aA}	0.90 ± 0.04 ^{aA}	0.90 ± 0.03 ^{aA}
14	1.18 ± 0.04 ^{bB}	1.02 ± 0.04 ^{aB}	1.20 ± 0.04 ^{bB}	0.99 ± 0.05 ^{aB}
28	1.39 ± 0.03 ^{cC}	1.23 ± 0.05 ^{abC}	1.29 ± 0.03 ^{bC}	1.20 ± 0.04 ^{aC}
Peroxide value [meq·kg⁻¹]				
0	1.82 ± 0.12 ^{aA}	1.74 ± 0.08 ^{aA}	1.88 ± 0.14 ^{aA}	1.94 ± 0.10 ^{aA}
14	3.22 ± 0.23 ^{bB}	2.33 ± 0.17 ^{aB}	2.50 ± 0.21 ^{aB}	3.06 ± 0.24 ^{bB}
28	7.66 ± 0.32 ^{bC}	5.85 ± 0.34 ^{aC}	6.22 ± 0.28 ^{abC}	7.24 ± 0.24 ^{bC}
TBARS values [mg·kg⁻¹]				
0	0.46 ± 0.02 ^{dA}	0.27 ± 0.02 ^{aA}	0.32 ± 0.02 ^{bA}	0.40 ± 0.03 ^{cA}
14	0.81 ± 0.04 ^{cB}	0.44 ± 0.02 ^{aB}	0.48 ± 0.02 ^{abB}	0.69 ± 0.02 ^{bB}
28	1.77 ± 0.12 ^{cC}	1.04 ± 0.07 ^{aC}	1.25 ± 0.08 ^{bC}	1.64 ± 0.14 ^{cC}

Data are expressed as mean ± standard deviation. Different lowercase letters in superscript indicate significant difference at $p < 0.05$ level between different formulations, while different uppercase letters in superscript are indicative of the same within each formulation during the storage period.

Acid value is expressed as grams of KOH. Peroxide value is expressed as milliequivalents of active oxygen. TBARS – thiobarbituric acid reactive substances (expressed as milligrams of malondialdehyde).

MC – control mayonnaise, MBHT – mayonnaise made with 1 g·l⁻¹ butylated hydroxytoluene addition, MDSB5 – mayonnaise made with sunflower oil macerated with 50 g·l⁻¹ dried sea buckthorn pomace, MDSB10 – mayonnaise made with sunflower oil macerated with 100 g·l⁻¹ dried sea buckthorn pomace.

MBHT, MDSB5 and MDSB10 were 3.80, 3.93, 3.88 and 3.90 respectively.

The acid value is a measure of the amount of free fatty acids, which were produced by the oxidation of double bonds of unsaturated fatty acid esters due to the action of oxidative enzymes, and by hydrolysis from triacylglycerols due to the action of lipolytic enzymes. Immediately after processing, no significant differences were observed in *AV* between control and experimental samples. The *AV* increased gradually in all samples during storage. At day 28, the highest mean *AV* was found in the control mayonnaise, while the MDSB10 mayonnaise had the lowest *AV*, lower than the BHT-treated sample. These findings are in agreement with previous studies investigating the effect of mayonnaise enrichment with natural plant materials, such as extracts and powders, on the oxidative stability during storage [28].

Mayonnaise is susceptible to deterioration through lipid oxidation due to the large surface area of the oil-in-water emulsion droplets that facilitates interactions between the oil and water-soluble pro-oxidants [29]. *PV* determines the primary oxidation products (hydroperoxides) formed during the autoxidation of unsaturated lipids and it is an indicator of the initial stage of lipid oxidation or oxidative rancidity [28, 30]. After preparing the mayonnaises (day 0), the highest *PV* value was obtained in MDSB10 samples ($1.94 \text{ meq}\cdot\text{kg}^{-1}$). However, no significant differences were found between *PV* values of mayonnaise samples at this moment. ANOVA indicated a significant ($p < 0.05$) increase in the *PV* value of mayonnaise with storage. The results confirmed the previous finding that *PV* increased gradually in control and experimental samples throughout the storage period [1, 31, 32]. As can be seen in Tab. 3, control mayonnaise showed the highest *PV* both after 14 days ($3.22 \text{ meq}\cdot\text{kg}^{-1}$) and at the end of storage ($7.66 \text{ meq}\cdot\text{kg}^{-1}$).

The results also showed that BHT retarded the hydroperoxide formation significantly ($p < 0.05$) in mayonnaise throughout 28 days of storage, indicating the high efficiency of BHT in retarding lipid oxidation. *PV* of MDSB5 and MDSB10 samples were lower compared to the control sample but the lowest *PV* values were recorded in MBHT samples (Tab. 3). Carotenoids, as hydrophobic antioxidants, could have higher efficiency than hydrophilic antioxidants in the prevention of oxidation in oil-in-water emulsion systems. However, several previous studies showed that carotenoids can act as both antioxidants and pro-oxidants under different conditions [33]. In the process of lipid peroxidation, they may act as pro-oxidants

depending on their intrinsic properties and concentration, as well as on the redox potential of the biological environment in which they act. This behaviour occurs in particular at high carotenoid concentrations or at high partial pressures of oxygen and depends on the interactions with other antioxidants such as α -tocopherol, vitamin C or polyphenols [34, 35]. The higher *PV* of MDSB10 as compared with MDSB5 was probably due to the higher content of carotenoids in these samples.

The results of the secondary lipid oxidation products, as shown by the *TBARS* values, are presented in Tab. 3. Storage time had a significant effect on mayonnaise oxidation, an increasing level of *TBARS* was observed in all samples over the storage period, indicating an increase in lipid oxidation during storage. The greatest increase in *TBARS* values was observed in control mayonnaise samples, the *TBARS* value at the end of the storage period being 3.8-fold higher in these samples. The *TBARS* values of MDSB5 samples were significantly lower ($p < 0.05$) than in control samples throughout the storage period, thus indicating the protective effect of carotenoids extracted from dried sea-buckthorn pomace against lipid oxidation in mayonnaise. However, the strongest protective effect was observed for BHT. After 28 days of storage, *TBARS* values of MDSB10 samples were lower than those of the controls but the differences were not significant.

Therefore, the efficacy of carotenoids in retarding lipid oxidation was highly dependent on concentration. KIOKIAS et al. [36] showed also that carotenoid concentration may affect, alongside carotenoid and emulsion structure, the carotenoid activity in sunflower oil-in-water emulsions.

The results of the sensory analysis of the mayonnaise samples after preparation as well as after 14 and 28 days of storage at 4 °C are shown in Tab. 4. Except for colour, the sensory attributes of MC, MBHT, MDSB5 and MDSB10 samples were not significantly ($p < 0.05$) affected at zero time, showing that the enrichment of mayonnaise with carotenoids after extraction of DSB in the oil did not significantly influence the taste, consistency and the overall acceptability of mayonnaise. A significant decline in all sensory attributes and overall acceptability of mayonnaise was observed during storage. A similar trend for colour, aroma, taste and overall acceptability were previously observed during the storage of control and lycopene-added mayonnaise [31]. Regarding colour, the highest score was recorded for MDSB5 sample throughout the storage period, proving that the more intense yellow colour of the mayonnaise made from oil enriched with carotenoids from

Tab. 4. Effect of storage on sensory attributes of mayonnaise samples.

Storage time [d]	MC	MBHT	MDSB5	MDSB10
Colour				
0	8.08 ± 0.51 ^{aC}	8.17 ± 0.58 ^{aC}	8.67 ± 0.49 ^{bC}	7.92 ± 0.67 ^{aC}
14	7.25 ± 0.62 ^{aB}	7.75 ± 0.45 ^{bcB}	8.17 ± 0.58 ^{cB}	7.58 ± 0.51 ^{abB}
28	6.25 ± 0.45 ^{aA}	7.25 ± 0.45 ^{bA}	7.58 ± 0.51 ^{bA}	6.58 ± 0.67 ^{aA}
Taste				
0	8.33 ± 0.49 ^{aC}	8.42 ± 0.51 ^{aC}	8.50 ± 0.52 ^{aC}	8.33 ± 0.65 ^{aC}
14	7.08 ± 0.67 ^{aB}	7.50 ± 0.67 ^{abB}	7.67 ± 0.49 ^{bB}	7.25 ± 0.62 ^{abB}
28	6.08 ± 0.51 ^{aA}	6.83 ± 0.39 ^{bA}	7.17 ± 0.58 ^{bA}	6.33 ± 0.49 ^{aA}
Consistency				
0	8.25 ± 0.45 ^{aC}	8.33 ± 0.49 ^{aC}	8.42 ± 0.51 ^{aC}	8.33 ± 0.65 ^{aC}
14	7.17 ± 0.39 ^{aB}	7.42 ± 0.51 ^{abB}	7.58 ± 0.51 ^{bB}	7.25 ± 0.45 ^{abB}
28	5.92 ± 0.51 ^{aA}	6.58 ± 0.34 ^{bA}	6.50 ± 0.52 ^{bA}	6.17 ± 0.58 ^{abA}
Overall acceptability				
0	8.25 ± 0.45 ^{aC}	8.33 ± 0.49 ^{aC}	8.42 ± 0.51 ^{aC}	8.17 ± 0.72 ^{aC}
14	7.17 ± 0.58 ^{aB}	7.58 ± 0.51 ^{bB}	7.67 ± 0.49 ^{bB}	7.33 ± 0.49 ^{abB}
28	6.17 ± 0.39 ^{aA}	7.00 ± 0.43 ^{bA}	7.17 ± 0.39 ^{bA}	6.33 ± 0.65 ^{aA}

Data are expressed as mean ± standard deviation. Different lowercase letters in superscript indicate significant difference at $p < 0.05$ level between different formulations, while different uppercase letters in superscript are indicative of the same within each formulation during the storage period.

MC – control mayonnaise, MBHT – mayonnaise made with 1 g·l⁻¹ butylated hydroxytoluene addition, MDSB5 – mayonnaise made with sunflower oil macerated with 50 g·l⁻¹ dried sea buckthorn pomace, MDSB10 – mayonnaise made with sunflower oil macerated with 100 g·l⁻¹ dried sea buckthorn pomace.

50 g·l⁻¹ dried sea-buckthorn pomace was appreciated by the panelists. However, the deep-yellow colour of MSB10 samples was less appreciated and, as a result, the overall acceptability of these samples was lower (Fig. 2). Evaluation of all sensory attributes showed that MDSB5 was the most favourable sample and had the highest scores throughout the storage, eventually better than the BHT-treated sample. However, there was no difference in all attributes among MDSB5 and BHT-treated samples ($p > 0.05$). Both after 14 and 28 days of storage, the lowest scores were given to the control sample for all the sensory properties, which was probably due to the darkening as well as to the off-flavours and off-odours generated in the deteriorative reactions of lipids that occurred during storage. This was in accordance with the higher increase of *PV* and *TBARS* values in this sample, indicating that lipid oxidation proceeded to a greater extent.

CONCLUSIONS

The use in the manufacture of mayonnaises of a vegetable oil enriched with carotenoids directly extracted in the oil from by-products of

sea buckthorn processing led to the improvement of chromatic characteristics of mayonnaise, without significantly affecting its taste, consistency and the overall acceptability. The mayonnaise enriched with carotenoids from extraction of 50 g·l⁻¹ dried sea buckthorn pomace in the oil exhibited a better oxidative stability during storage as indicated by lower *PV* and *TBARS* values. However, a higher carotenoid content of the oil, as a result of the extraction from 100 g·l⁻¹ dried sea buckthorn pomace, could affect the physico-chemical and sensory characteristics of mayonnaise during storage, probably due to the pro-oxidant behaviour of carotenoid. By using sunflower oil enriched with carotenoids after extraction from 50 g·l⁻¹ dried sea-buckthorn pomace, a stable and safe mayonnaise can be produced without adding synthetic antioxidants, while valorizing sea buckthorn by-products.

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