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## Research Article

# Enhancement the Stability, Quality and Functional Properties of Rapeseed Oil by Mixing with Non-conventional Oils

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## Abstract

**Objective:** The main target of this study was to raise stability, quality and functional properties of rapeseed oil by mixing with non-conventional oils, namely apricot kernels, grape seed, tomato seed and wheat germ containing high levels of phytonutrients. **Methodology:** These components such as tocopherols, tocotrienols and phytosterols as well as fatty acid composition were determined by HPLC and GLC. Rancimat was used for detecting oxidative stability. **Results:** Admix rapeseed oil (95, 90 and 80% v/v) with four non-conventional oils resulted in a decrease in the ratio of polyunsaturated/saturated fatty acids which have a positive influence on oxidative stability. The ratio of omega-6 to omega-3 in mixed oils was attained to desirable ratios having positive effects in decrease the risk of some diseases. Oxidative stability of rapeseed oil blended with wheat germ oil was highest. The amount of  $\beta$ -sitosterol was increased by increasing the ratios of non-conventional oils. Adding wheat germ oil to rapeseed oil leads to an increase in total tocopherols and  $\alpha$ -tocopherol. **Conclusion:** Admixed rapeseed oil with non-conventional oil at a level of 20% v/v is more satisfactory and superior to other blends in terms of stability which is an important indicator the oil quality and shelf life of edible oils.

**Key words:** Phytonutrients, tocopherols, tocotrienols, phytosterols, oxidative stability, quality, functional properties

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**Competing Interest:** The authors have declared that no competing interest exists.

**Data Availability:** All relevant data are within the paper and its supporting information files.

## INTRODUCTION

Food industries produce huge quantities of by-products<sup>1</sup>, estimated to be around 800000 t year<sup>-1</sup>. These residues are highly perishable products that are difficult to manage because of environmental problems in the industries<sup>2</sup>. An interesting approach to providing an added value to by-products is their use as sources of plant oils, particularly since; they are containing unique bioactive compounds.

Tomato (*Lycopersicon esculentum* MILL., Solanaceae) is the most important vegetable juice in terms of per capita consumption. During tomato juice pressing about 3-7% of the raw material is lost as waste<sup>3</sup>. Tomato seed oil has attracted interest since it is rich in  $\gamma$ -tocotrienol<sup>4</sup>.

Grapes (*Vitis* sp., Vitaceae) are the largest worldwide fruit crop with more than 60 million tons produced per annum. About 80% of the total crop is used in wine processing leads to producing about 9 million tons of pomace per year<sup>5</sup>. Grape seed oil has a high content of  $\alpha$ -tocotrienol<sup>4</sup>.

Apricots (*Prunus armeniaca* L., Rosaceae) are an internationally popular fruit crop, with the global production reaching 4 million tons in 2012<sup>6</sup>. The large consumption of apricot, fresh fruits, juice, jam and dried fruits, produces higher quantities of kernels as by-products. Apricot kernels contain about 40-50% of oil; it has a like composition to almond oil<sup>7</sup>. Apricot kernel oil characterized by presenting of oleic as a major fatty acid followed by linoleic and palmitic acids as well as higher values in gamma-tocopherol<sup>4</sup>.

Wheat germs (*Triticum aestivum*) are one of the main by-products of the wheat milling industry and are generally used for animal feeding. In addition, wheat germ containing about 8-14% of oil and it is rich in omega-6 and omega-3 fatty acids as well as  $\alpha$ -tocopherol<sup>4,8</sup>.

Total international consumption of plant oils has increased by 3.6% to 176 million tons in 2011, from 170 million tons in 2010. More than 50% of the increase was used in the food industry to meet requesting from a growing population, leaving only 2.4 million tons for the energy market and oleochemical industry<sup>9</sup>. In 2013/2014, the global rapeseed oil consumption amounted to 26 million metric tons, up from 11 million metric tons in 1995/1996. The oxidative stability of rapeseed oil is rather limited because of the high content of unsaturated fatty acids. Blending rapeseed oil with non-conventional plant oils obtained from by-products could increase its oxidative stability and decrease the amount of wastes generated by the food industry.

The research field of food science and technology still met big challenges in finding other sources of edible oils (e.g., from food industry by-products) as well as alternative

methods of add value to produce food materials, furthermore to keeping their stability, quality and safety.

Therefore, this study aimed to utilize the four non-conventional oils (apricot kernels, grape seed, tomato seed and wheat germ) recovered from food industries by-products at ratios 5, 10 and 20% v/v to fortified rapeseed oil. Phytonutrient components, fatty acid composition and oxidative stability of oil blends were determined using GLC, HPLC and Rancimat.

## MATERIALS AND METHODS

**Materials:** Rapeseed oil was purchased from commercial retail outlet in Poland. A freshly milled wheat germ was supplied by The Milling Organization, North Cairo, Egypt as a by-product of wheat milling process. Grape pomace, a by-product containing grape seeds was obtained from the Egyptian Vineyards and Distilleries Company (Ginaclis, Alexandria, Egypt). Apricot kernels were received from Food Canning Factories, Egypt. Tomato waste containing of skin and seeds were obtained from Kaha Factory, Egypt. All previous seeds (season 2013) were cleaned, dried and the lipids from all above seeds were extracted with n-hexane in laboratory conditions.

All solvents of HPLC grade, 1 M methanolic KOH, sterol standards and anhydrous pyridine were purchased from Sigma-Aldrich (St. Louis, MO, USA). Standards of tocopherols were obtained from Calbiochem-Novobiochem (San Diego, CA, USA), FAME standards and Sylon BTZ was purchased from Supelco (Bellefonte, PA, USA).

**Preparation of vegetable oil blends:** Rapeseed oil was blended with either of apricot kernel oil, grape seed oil, tomato seed oil or wheat germ oil in the following weight ratios: (95:5), (90:10) and (80:20).

### Methods

**Fatty acids:** Methyl esters of fatty acids (FAME) were prepared according to AOCS Official method<sup>10</sup> Ce 1k-07.

**Phytosterols:** Sterol content and composition were determined by GC following the procedure described by AOCS Official method<sup>11</sup> Ch 6-91.

**Tocochromanols:** The determination of tocochromanols (tocopherols and tocotrienols) according to Balz *et al.*<sup>12</sup>.

**Oxidative stability index:** Oxidative stability of oils was determined using the AOCS Official method<sup>13</sup> Cd 12b-92.

Table 1: Phytosterols and phytostanols contents in blended oils

Rapeseed oil blended with oils from												
Phytosterols	Apricot kernels			Grape seeds			Tomato seeds			Wheat germ		
	5%	10%	20%	5%	10%	20%	5%	10%	20%	5%	10%	20%
Cholesterol	Nd	Nd	Nd	Nd	Nd	Nd	0.04±0.01	0.06±0.01	0.13±0.01	Nd	Nd	Nd
Brassicasterol	0.60±0.02	0.59±0.02	0.49±0.02	0.57±0.03	0.55±0.02	0.45±0.02	0.53±0.02	0.48±0.02	0.44±0.02	0.63±0.03	0.52±0.02	0.49±0.02
Campesterol	1.86±0.13	1.84±0.14	1.54±0.13	1.79±0.13	1.76±0.12	1.42±0.12	1.67±0.14	1.58±0.12	1.91±0.15	2.48±0.19	2.38±0.19	3.03±0.22
Campestanol	0.14±0.01	0.16±0.01	0.12±0.01	0.13±0.01	0.11±0.01	0.11±0.01	0.13±0.01	0.09±0.01	0.15±0.01	0.14±0.01	0.18±0.01	0.18±0.01
Δ5-stigmasterol	0.03±0.01	0.04±0.01	0.04±0.01	0.03±0.01	0.05±0.01	0.08±0.01	0.04±0.01	0.04±0.01	0.07±0.01	0.03±0.01	0.06±0.01	0.05±0.01
β-sitosterol	2.70±0.22	2.75±0.21	2.59±0.20	2.57±0.21	2.60±0.22	2.64±0.19	2.51±0.15	2.86±0.21	3.35±0.27	3.87±0.27	4.13±0.29	5.72±0.30
Sitostanol	0.06±0.01	0.09±0.01	0.06±0.01	0.06±0.01	0.06±0.01	0.06±0.01	0.07±0.01	Nd	Nd	0.05±0.01	0.09±0.01	0.10±0.02
Δ5-avenasterol	0.06±0.01	0.10±0.01	0.10±0.01	0.09±0.01	0.09±0.01	0.10±0.01	0.10±0.01	0.12±0.01	0.11±0.01	0.16±0.02	0.17±0.02	0.27±0.03
Cycloartenol	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.07±0.01	0.09±0.01	0.13±0.01
Δ7-stigmasterol	Nd	Nd	Nd	Nd	Nd	Nd	0.08±0.01	0.16±0.01	0.19±0.01	0.08±0.01	0.10±0.01	0.11±0.01
24 methylene-cycloartenol	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.02±0.01	0.02±0.01	0.04±0.01
Citrostadienol	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.02±0.01	0.03±0.01	0.04±0.01
Others	Nd	0.02±0.01	0.02±0.01	0.03±0.01	0.02±0.01	0.05±0.01	0.06±0.01	0.04±0.01	Nd	0.04±0.01	Nd	0.13±0.01
Total	5.45	5.59	4.96	5.27	5.24	4.91	5.23	5.43	6.35	7.57	7.77	10.29

Nd: Not detected

The protective factor of the blended oils, expressed as the extension of the induction period<sup>14</sup> was calculated as percentage following the equation:

$$PF = (IP \text{ blended oil} - IP \text{ rapeseed oil}) \times 100 / IP \text{ rapeseed oil}$$

**Statistical analysis:** Results are presented as the Mean±standard deviation from three replicates of each experiment. A  $p < 0.05$  was used to denote significant differences between mean values determined by the analysis of variance (ANOVA) with the assistance of Statistica 7.0 software (Stat Soft Inc., Tulsa, OK).

## RESULTS AND DISCUSSION

Table 1 shows the phytosterol and phytostanol composition for rapeseed oil blended with oils extracted from by-product. Phytosterols of rapeseed oil are comprised of brassicasterol (0.642 mg g<sup>-1</sup>), campesterol (1.241 mg g<sup>-1</sup>), β-sitosterol (1.443 mg g<sup>-1</sup>) and D5-avenasterol (0.05 mg g<sup>-1</sup>) and phytostanols, campestanol (0.12 mg g<sup>-1</sup>) and sitostanol (0.05 mg g<sup>-1</sup>). The β-sitosterol, the major sterol of most vegetable oils was also the major constituent of non-conventional investigated oils. From the results recorded in Table 1, it was observed that β-sitosterol increased from 1.4 mg g<sup>-1</sup> in rapeseed oil to 2.7, 2.75, 2.59 mg g<sup>-1</sup> and 2.57, 2.60, 2.64 mg g<sup>-1</sup> as well as 2.51, 2.86, 3.35 mg g<sup>-1</sup> when 5, 10 and 20% were added from apricot kernel, grape seeds and tomato seeds oils to rapeseed oil, respectively. Meanwhile, β-sitosterol reached the highest level in the case

of 5, 10 and 20% addition from wheat germ oil to rapeseed oil (3.87, 4.14 and 5.72 mg g<sup>-1</sup>, respectively). In addition, cycloartenol, 24-methylene-cycloartenol and citrostadienol were found in reasonable amounts in oil blends with wheat germ oil (5, 10 and 20%) which are not ultimately found in individual rapeseed oil. Also, Δ7-stigmasterol was detected in rapeseed oil when it was blended with wheat germ oil or tomato seed oil.

When rapeseed oil blended with non-conventional oils leads to an increase of β-sitosterol levels. Kakade and Magdum<sup>15</sup> reported that β-sitosterol is known to control cholesterol levels, reduce the activity of cancer cell, promote prostate gland health and enhance immunity in the human body. The β-sitosterol, campesterol and stigmasterol exert antioxidant effects. Polymerization of oils can be inhibited by presence of 5-avenasterol during heating treatments<sup>16</sup>.

The tocochromanols profiles of the four oil blends under investigation are shown in Table 2. Individual rapeseed oil contained an appreciable amount of α-tocopherol (0.32 mg g<sup>-1</sup>) and γ-tocopherol at 0.35 mg g<sup>-1</sup> with a percentage value of 46.3 and 50.7%, respectively. Concerning the total tocopherols in single rapeseed oil is amount to 0.69 mg g<sup>-1</sup> and the total contents of tocopherols in blended oils, it could be noticed that the addition of wheat germ oil to rapeseed oil provided the highest content of total tocopherols. Concerning the tocopherols composition, an addition of wheat germ oil to rapeseed oil resulted in the highest content of α-tocopherol (0.38, 0.47 and 0.68 mg g<sup>-1</sup>). Concerning γ-tocopherol the addition of apricot kernel oil to rapeseed oil provided its slight increase. Concerning

Table 2: Tocochromanols contents in blended oils (mg g<sup>-1</sup>)

Rapeseed oil blended with oils from												
Tocochromanols	Apricot kernels			Grape seeds			Tomato seeds			Wheat germ		
	5%	10%	20%	5%	10%	20%	5%	10%	20%	5%	10%	20%
α-tocopherol	0.29±0.01	0.28±0.01	0.26±0.01	0.30±0.01	0.29±0.01	0.26±0.01	0.31±0.01	0.27±0.01	0.25±0.01	0.38±0.02	0.47±0.02	0.68±0.03
α-tocotrienol	Nd	Nd	Nd	Nd	0.01±0.00	0.02±0.00	Nd	Nd	Nd	Nd	Nd	Nd
β-tocopherol	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.04±0.01	0.07±0.01	0.16±0.01
γ-tocopherol	0.41±0.02	0.42±0.02	0.43±0.01	0.34±0.02	0.33±0.02	0.30±0.02	0.33±0.02	0.32±0.02	0.27±0.01	0.40±0.01	0.36±0.01	0.34±0.01
γ-tocotrienol	Nd	Nd	Nd	Nd	0.01±0.00	0.02±0.00	0.06±0.01	0.13±0.01	0.27±0.01	Nd	Nd	Nd
δ-tocopherol	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	Nd	Nd
Total	0.71	0.71	0.70	0.65	0.65	0.61	0.71	0.73	0.80	0.83	0.90	1.18

Nd: Not detected

Table 3: Fatty acid composition of blended oils (%)

Rapeseed oil blended with oils from												
Fatty acids	Apricot kernels			Grape seeds			Tomato seeds			Wheat germ		
	5%	10%	20%	5%	10%	20%	5%	10%	20%	5%	10%	20%
16:0	4.5±0.2	4.5±0.2	4.7±0.2	4.8±0.2	5.0±0.2	5.3±0.3	5.1±0.2	5.6±0.1	6.3±0.2	5.2±0.2	5.8±0.3	7.3±0.3
16:1	0.4±0.1	0.5±0.1	0.6±0.1	0.4±0.1	0.4±0.1	0.5±0.1	0.3±0.1	0.3±0.1	0.4±0.1	0.4±0.1	0.4±0.1	0.3±0.1
18:0	1.6±0.1	1.6±0.1	1.5±0.1	1.8±0.1	1.8±0.1	2.1±0.1	1.8±0.1	1.8±0.1	2.10.10	1.5±0.1	1.5±0.1	1.4±0.1
18:1	62.3±3.2	62.6±3.1	62.9±3.2	58.9±2.9	58.2±2.5	54.1±2.2	60.2±2.6	58.3±2.1	54.1±2.3	59.5±2.2	58.0±2.4	52.8±2.1
18:2	20.7±1.5	20.6±1.3	21.0±1.1	22.3±1.0	24.9±1.1	29.6]±1.3	21.8±1.0	24.4±1.0	27.2±1.2	21.9±0.9	24.0±1.1	27.4]±1.2
18:3	8.9±0.5	8.4±0.5	7.8±0.4	9.1±0.4	8.5±0.4	8.1±0.4	9.0±0.1	8.4±0.1	8.0±0.1	9.1±0.1	9.0±0.1	9.0±0.1
20:0	0.4±0.1	0.4±0.1	0.4±0.1	0.3±0.1	0.3±0.1	0.3±0.1	0.3±0.1	0.4±0.1	0.3±0.1	0.3±0.1	0.3±0.1	0.4±0.1
20:1	1.0±0.1	0.8±0.1	0.7±0.1	0.9±0.1	0.9±0.1	0.7±0.1	0.9±0.1	0.8±0.1	0.7±0.1	1.0±0.1	0.9±0.1	0.9±0.1
SFA	6.5	6.5	6.6	6.9	7.1	7.7	7.2	7.8	8.7	7.0	7.6	9.1
MUFA	63.7	63.9	64.2	60.2	59.5	55.3	61.4	59.4	55.2	60.9	59.3	54.0
PUFA	29.6	29.0	28.8	31.4	33.4	37.7	30.8	32.8	35.2	31.0	33.0	36.4
PUFA/SFA	4.5	4.5	4.4	4.6	4.7	4.9	4.3	4.2	4.0	4.4	4.3	4.0
n-6/n-3	2.3	2.5	2.7	2.5	2.9	3.7	2.4	2.9	3.4	2.4	2.7	3.0

Fatty acids composition of rapeseed oil as follows<sup>22</sup>: 16:0 = 4.6, 16:1 = 0.4, 18:0 = 1.7, 18:1 = 62.2, 18:2 = 20.0, 18:3 = 9.4, 20:0 = 0.3, 20:1 = 0.9, SFA: Saturated fatty acids, MUFA: Monounsaturated fatty acids, PUFA: Polyunsaturated fatty acid, n-6/n-3: Omega 6/omega 3

Table 4: Oxidative stability of blended oils

Rapeseed oil blended with oils												
Oxidative factors	Apricot kernels			Grape seeds			Tomato seeds			Wheat germ		
	5%	10%	20%	5%	10%	20%	5%	10%	20%	5%	10%	20%
Induction period (h)	18.5±0.5	19.8±0.5	23.6±0.5	15.1±0.3	14.5±0.3	12.7±0.2	17.3±0.3	18.4±0.4	17.9±0.3	28.6±0.5	33.8±0.6	34.7±0.6
Protective factor (%)	19.4	27.7	52.3	-2.6	-6.5	-18.1	11.6	18.7	15.5	84.5	118.1	123.9

γ-tocotrienol it was not found in individual rapeseed oil but when it was mixed with grape seed and tomato seed oils (10 and 20 w/w), it was found that reasonable amount. Recently, research indicated that tocotrienols are important for human health due to their activity as hypocholesterolemic and antioxidant compounds<sup>17</sup> and as a hepatoprotection<sup>18</sup>.

Fatty acid composition of investigated oil blends is presented in Table 3. Generally, in rapeseed oil blended with other oils at different ratios a noticeable alteration was observed in saturated and unsaturated fatty acids. It was found that the PUFA/SFA ratio of blended rapeseed oil with non-conventional oil decreased to 4.0 in case of 20% tomato seed and wheat germ oils, which have a positive influence on

oxidative stability. It is well known that the PUFA/SFA ratio is usually taken as a measure of the tendency of oils to undergo oxidation<sup>19,20</sup>. The omega-6 to omega-3 ratio in blended oils reached desirable ratios, as recorded in Table 3, having positive effects in reducing the risk of some diseases. Simopoulos<sup>21</sup> reported that the optimal omega-6/omega-3 ratio ranges from 1:1-4:1, depending on the disease under consideration.

The oxidative stability of oils and fats is one of the most important parameters for their quality assessment. The Rancimat method measures the Induction Period (IP) which is the period that precedes the main oxidation process<sup>23</sup>. Table 4 indicates IP (h) for all the examined blending oils. The

IP of the rapeseed oil was 15.5 h and the highest IP values were reached at 28.6, 33.8 and 34.7 h with wheat germ oil blends followed by apricot kernel oil (18.5, 19.8 and 23.6 h), then tomato seed oil and grape seed oil. The IPs of the blended oils were in the following order: Rapeseed oil with wheat germ oil > rapeseed oil with apricot kernel oil > rapeseed oil with tomato seed oil > rapeseed oil with grape seed oil. It was found that the oxidative stability of oil blends depended upon the PUFA to SFA ratio and the total tocopherol content in the oil blends. Non-conventional oil with rapeseed oil showed marked improvement in the oxidative stability in comparison to pure rapeseed oil. An increase in the amount of non-conventional oils in the blends has been reported to cause a drastic increase in the oxidative stability and protective factor except for grape seed oil blends. On the other hand, an addition of grape seed oil to rapeseed oil improved the levels of phytonutrient components, which it is very important from the nutritional point of view.

### CONCLUSION

It is clear from the composition of vegetable oils, that no single oil meets all the oil nutritional requirements of essential fatty acids, micronutrients components, fatty acid composition and vitamins. The rapeseed oil can be blended even to derive the protective advantage due to the presence of specific ingredients, offering protection against oxidation to improve stability, quality and functional properties. The principal finding of this study is the value added to rapeseed oil by incorporating non-conventional oils due to the presence of highly beneficial phytonutrients components. Also, blended rapeseed oil and non-conventional vegetable oils lead to lower PUFA/SFA ratio and an increase of total tocopherol contents, thus increasing the oxidative stability of the oils. The blended oils have several advantages e.g., an increase oxidative stability which is an important indicator determining oil quality and shelf life.

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