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Comparative Evaluation of Physical and Physicochemical Properties and Antioxidant Potential of Various Cooking Oils

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The study was based on the comparative evaluation of physical and physicochemical properties and antioxidant potential of different cooking oils as awareness for the consumers. The cooking oils extracted from sunflower, corn, canola, soybean, and rapeseed and available for consumers as different commercial brands were purchased from the local market and analysed for their physical, physicochemical and antioxidant properties. All of the selected oils were found to be statistically similar on the basis of their physical properties including odour, specific gravity (*P*=.65) and refractive index (*P*=0.84). All of the selected oils contained vitamin A except one brand of each of the sunflower, corn and canola oils. The selected oils and their blend showed statistically different physicochemical properties and antioxidant potential (*P*=.000). The corn oil and rapeseed oil were found to be the best quality oil due to comparatively lower acid, peroxide and

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saponification values and higher antioxidant potential in terms of free radical scavenging capacity. The study results would provide valuable information to the consumers and the researchers regarding the selection of the best quality cooking oils available in the market.

Keywords: Cooking oils; physical properties; physicochemical properties; antioxidant potential; vitamin A; free radical scavenging capacity.

1. INTRODUCTION

Plant seed oils are categorized as simple lipids which are liquid at room temperature due to the presence of unsaturated fatty acids. However, some of the plant oils such as coconut oil, palm oil and palm kernel oil are rich in saturated fatty acids and thus solidify at room at relatively lower temperature. Plant seed oils also known as vegetable oils or cooking oils including olive oil, sunflower oil, corn oil, canola oil, soybean oil, rapeseed oil and peanut oil are generally used for frying, baking, cooking foods and salad dressings. During frying and cooking, these oils provide a medium for the transfer of heat and give texture and flavour to food products. The nutritional and edible quality of the cooking oils depends on its chemical composition and its stability in moisture and high temperature [1,2].

The oils are basically composed of triacylglycerol and free fatty acids. They also contain some other components like phospholipids, sterols, triterpene alcohols, carotenes, chlorophylls, colouring matters, hydrocarbons, metals, unwanted flavours and oxidant products [3]. These also contain traces of hydrocarbons including alkanes, alkenes, carotenes and polycyclic hydrocarbons. The carotenes are important minor components of many vegetable oils like palm oil and give yellowish, red or orange colour to the oil [4].

The chemical and physicochemical composition of the cooking oil significantly affects its nutritional and edible quality. The oils containing unsaturated fatty acids, preferably the polyunsaturated omega-3 fatty acids are considered as beneficial for human health as they are easily transported via blood in the form of high-density-lipoproteins [5]. However, the oils composed of fatty acids with a high degree of unsaturation are at more risk of hydrolytic and oxidative rancidity and show relatively higher acid and peroxide values. Therefore, the higher the degree of unsaturation in the oil, the higher would be the acid and peroxide value and the lower would be its edible quality. On the other hand, the lower the degree of unsaturation in the oil, the lesser would be its stability towards polymerization during heating and lesser would be the risk of oxidative rancidity [6]. The oils showing higher saponification value contain short chain fatty acids and relatively lower content of essential fatty acids. Such types of oils also show higher acid value due to the release of a large number of fatty acids on rancidification [7]. However, the oils rich in antioxidant phytochemical compounds such as fat-soluble vitamins including tocopherol and vitamin A and polyphenols are more resistant to oxidative rancidity as they inhibit lipid peroxidation and have a relatively long shelf life [8].

Previously, several studies have been reported on the edible, nutritional and antioxidant quality of various plant oils [2,9–12]. However, limited data is available on the comparative evaluation of the said qualities of cooking oils supplied by various brands in Pakistan. It was therefore found necessary to plane a study on the comparative evaluation of the physical, physicochemical and antioxidant properties of different cooking oils supplied by various brands in Pakistan. The study would be a valuable source of information for the consumers and the researchers dealing with cooking oils.

2. MATERIALS AND METHODS

2.1 Chemicals and Reagents

Antimony trichloride, chloroform, hydrochloric acid, hydrogen peroxide, potassium iodide and sodium thiosulphate were purchased from Reidel-de-Haen (Germany), 2,2 diphenyl,1-picrylhydrazyl, glacial acetic acid, phenolphthalein, Trolox (6-hydroxyl-2,5,7,8-tetramethylchroman-2-carboxylic acid) from Fluka (United States) diethyl ether, ferrous sulphate pentahydrate, salicylic acid, starch from Sigma (St. Louis, United States) ethanol, methanol and potassium hydroxide from Merck (Germany) and hexane from Fischer Chemicals (Waldachtal, Baden-Wurttemberg, Germany).

2.2 Study Design

The oils extracted from various plants seed including sunflower, corn, canola, soybean oil and rapeseed and a blend of sunflower, soybean

and canola oil provided by different brands were purchased from the local market. The samples were brought to the research laboratory at the Institute of Chemical Sciences, Bahauddin Zakariya University, Multan, Pakistan and stored in airtight glass containers in sterilized and moisture free environment at 25±5°C. The oils and their blend were analysed for their physical properties including colour, odour, specific gravity and refractive index, physicochemical properties including saponification, acid and peroxide values and antioxidant potential in terms of free radical scavenging capacity. The flowsheet of the study design is presented in Fig. 1.

2.3 Physical Characteristics

The physical parameters including colour and odour of the oils were observed manually while the specific gravity and refractive index were determined using the previously reported method [13]. The specific gravity was determined by measuring the density of the oils using an empty clean pycnometer (10 ml) and calculated by the following expression.

$$Specific\ gravity = Density\ of\ oil / Density\ of\ water$$

The refractive index of the oil samples was determined by the reported method [14] using Abbe's refractometer. The oil samples were evaporated at the sodium vapour lamp at 20°C and refractive index was recorded.

2.4 Physicochemical Characteristics

The saponification value of different oil samples was determined by the standard method [15]. The oil sample (2 g) was mixed with alcoholic potassium hydroxide solution (25 ml). The contents were refluxed for 1 h with frequent shaking, followed the addition of 1% phenolphthalein solution (1 ml). The contents were titrated against 0.5M hydrochloric acid and saponification value was calculated using the following expression.

$$Saponification\ value\ (mg\ KOH\ g^{-1}\ oil) = (b - a) \times 28.05 / W_s$$

where a is the volume of hydrochloric acid used against the sample, b is the volume of hydrochloric acid against blank and W_s is the weight of the sample.

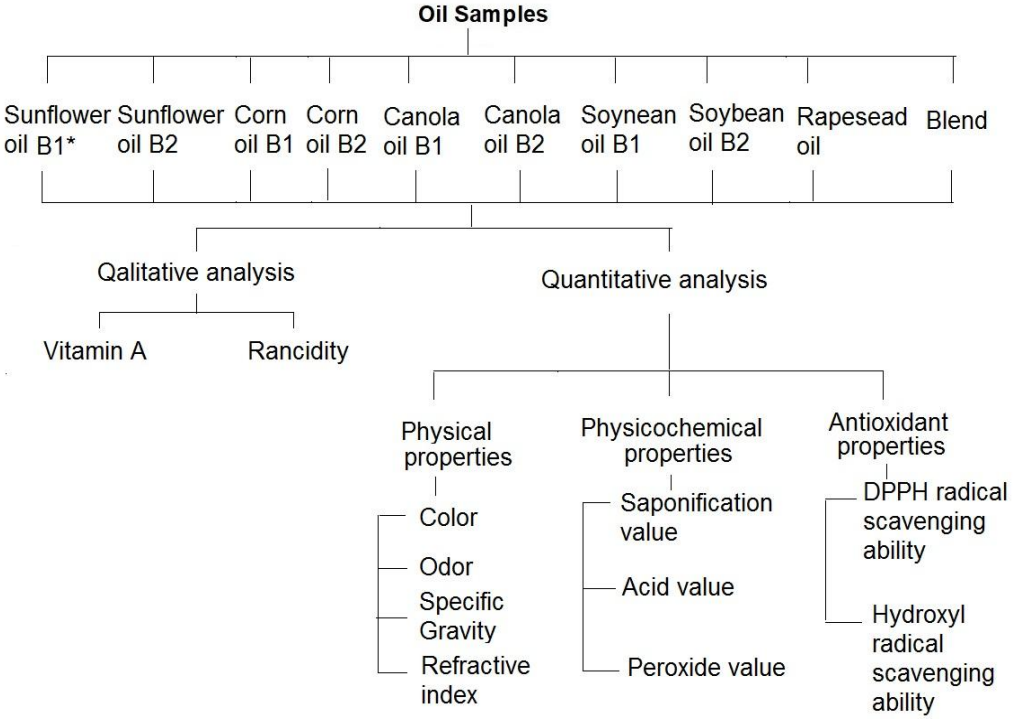

Fig. 1. Scheme of the study

**B1 and B2 indicate different brands using the oil from the seeds of the same plant*

The acid value of different oil samples was determined by the standard protocols as described by IUPAC [13]. The oil sample was mixed with freshly prepared mixture of diethyl ether and 95% ethanol (1:1 v/v) and 1 % phenolphthalein solution (1 ml). The mixture was titrated against 0.1 M sodium hydroxide solution followed by continuous shaking until a pink colour was obtained which persisted for 15 sec. The required volume of sodium hydroxide was noted and the acid value was calculated by the following expression.

$$Acid\ value\ (mg\ KOH\ g^{-1}\ oil) = Volume\ of\ NaOH\ used \times 5.61/W_s$$

where W_s is the weight of the sample.

The peroxide value was determined by the standard protocols [15]. The oil sample (1 g) was mixed with potassium iodide (1 g) and aqua solution (20 ml) prepared by mixing glacial acetic acid and chloroform (2:1 v/v). The mixture was placed in a boiling water bath for 30 sec followed by addition of 5% potassium iodide solution (20 ml) and 1% starch solution (1 ml). The contents were titrated against 0.002 M sodium thiosulphate solution. The procedure was also repeated with blank and the peroxide value was calculated using the following expression.

$$Peroxide\ value\ (mEqv.O_2Kg^{-1}\ oil) = M\ (V_s - V_b) \times 10\ mEq/W_s$$

where V_s is the volume of sodium thiosulphate solution used against the sample, V_b is the volume of Sodium thiosulphate solution used against a blank, *M* is the molarity of sodium thiosulphate solution and W_s is the weight of the sample.

2.5 Screening Tests

The presence of vitamin A in the oils was confirmed by the reported method [16]. The oil (2 g) was mixed with few drops of antimony trichloride reagent (25 ml of antimony trichloride mixed with 100 ml of chloroform). The appearance of green coloration in the mixture indicated the presence of vitamin A.

Rancidity of the oil sample was estimated by Kries test [17]. The oil sample (10 ml) was taken in a test tube and shaken vigorously with 0.1% phloroglucinol solution (10 ml) in ether and concentrated hydrochloric acid solution (10 ml) for 20 sec. The appearance of pink coloration indicated rancidity of oil samples.

2.6 Antioxidant Analysis

The antioxidant potential of the selected oils was determined in terms of hydroxyl radical scavenging capacity (OH-RSC) and 2, 2-diphenyl-1-picrylhydrazyl radical scavenging capacity (DPPH-RSC) following previously described protocols. OH-RSCS was determined using the salicylic acid method as reported earlier [18]. The oil sample (0.1 ml) was mixed with 95% ethanol (9.9 ml) followed by the addition of 1 ml of each of the salicylic acid (9 mM), hydrogen peroxide (8.8 mM) and ferrous sulfate hepta-hydrate (9 mM) solution. A mixture without sample was treated as control and that without salicylic acid as blank. The reaction mixture was allowed to stand at 37°C for 30 min and absorbance was recorded at 510 nm on a UV-visible spectrum (Jenway-6405, Japan). The OH-RSC was calculated using the following equation.

$$OH - RSC\ (\%) = [1 - (A_s - A_b)/A_c \times 100]$$

where A_s is the absorbance of sample A_b is the absorbance of blank, while A_c the absorbance of control.

DPPH-RSC was determined using the previously reported method [19] as described by Shad et al. with some modifications [11]. The oil sample (10 ml) was mixed with methanol (10 ml), mixed well and allowed to stand for 15 min. An aliquot (1 ml) from the methanolic layer was mixed with stable DPPH solution (3 ml) and allowed to react for 30 min at 25±5°C. The absorbance was recorded at 517 nm on a UV-visible spectrum (Jenway-6405, Japan) and DPPH-RSC was calculated by the following equation:

$$DPPH - RSC\ (\%) = [(A_s - A_b)/A_c] \times 100$$

where A_s is the absorbance of sampleA_b is the absorbance of blank, while A_c the absorbance of control.

2.7 Statistical Analysis

The result was expressed as mean± standard deviation of three parallel replicates. The means were separated by one-way analysis of variance (ANOVA) using Tukey's multiple range tests at 5% confidence level ($p \leq 0.05$).

3. RESULTS AND DISCUSSION

3.1 Physical Properties

The results of the physical properties of the selected oils and their blend are presented in Table 1. The oils were equally transparent without any turbidity, greenish yellow in colour and smelled an oily odour. However, the odour of the rapeseeds oil was found to be comparatively pungent than other ones. The specific gravity and refractive index of the selected oils ranged from 0.8990±0.001 to 0.9396±0.001 and 1.465± 0.001 to 1.469±0.001 respectively. The results for specific gravity and refractive index were found to be statistically similar (*P*= .65, .84 respectively) and comparable with those reported earlier [20,21]. The colour of cooking oils is due to the presence of carotenoids and few other pigments [22]. The specific gravity is inversely correlated with molecular weight and directly correlated with the degree of unsaturation in fats and oils. The refractive index is directly proportional to the number of carbon atoms in the fatty acids and gives a measure of fatty acids chain length in an oil [23]. The oils showing a relatively lower value of specific gravity and high value of refractive index are considered as good quality oil. The corn oil B1 and sunflower oil B1 were found to be good due to lower values of specific gravity and refractive index respectively.

3.2 Physicochemical Properties

The physicochemical properties of the selected oils were determined in terms of saponification value, acid value and peroxide value. The results for the physicochemical properties of the selected oils are given in Table 2. The saponification, acid and peroxide values of the oils ranged from 170.95±4.18 to 206.25 ±5.82, 0.324±0.013 to 1.328±0.183 and 5.10±0.424 to 18.40±0.283 mg KOH g^{-1} of oil respectively. A statistically significant variation (*P*= .00) in each of the studied physicochemical parameter was observed among the selected oils. The soybean oil B1, canola oil B1 and corn oil B1 showed comparatively lower saponification, acid and peroxide values respectively. The sunflower oil B1, sunflower oil B2 and canola oil B1 showed comparatively higher saponification acid and peroxide values respectively. The saponification and acid values of the oils were found to be within the standard range (92-250 mg KOH g^{-1} oil) while the acid values of sunflower oil B2, corn oil B2, canola oil B2, soybean B2 and the blend and peroxide values of sunflower oil B1, sunflower oil B2, canola oil B1 and soybean B1 were found to be higher than the standard value (0.6 mg KOH g^{-1} oil and 10 mEqv. of O_2 Kg^{-1} oil respectively) as recommended by Pakistan Standard Quality Control Authority (PSQCA) and Codex Alimentarius Commission [24].

Saponification value indicates the average chain length and molecular weight of the fatty acids present in the oil. The oils with higher the saponification, acid and peroxide values possess smaller chain length and molecular weight of fatty acids, are more susceptible to hydrolytic cleavage of triglycerides into fatty acid and undergo high extent of oxidative rancidity respectively [9,25]. In present study B1, canola oil B1 and corn oil B1oil was found to be the best due to low saponification, acid and peroxide values. The results are also comparable to those reported earlier [26]. The corn oil B1 and rapeseed oil were found to be the best with relatively lower values of each of the studied physicochemical parameter with no sign of rancidity.

Table 1. Physical properties of the selected oils and their blend

Oil	Colour	Odour	Specific gravity	Refractive index
Sunflower oil *B1	Greenish yellow	Fatty	0.9342.±0.013	1.465±0.012
Sunflower oil B2	Light yellow	Fatty	0.9396±0.021	1.469±0.011
Corn oil B1	Light yellow	Fatty	0.9339±0.014	1.467±0.009
Corn oil B2	Dark yellow	Fatty	0.9346±0.016	1.467±0.014
Canola oil B1	Yellow	Fatty	0.8990±0.043	1.466±0.021
Canola oil B2	Yellow	Fatty	0.9613±0.020	1.468±0.007
Soybean oil B1	Yellow	Fatty	0.9121±0.031	1.467±0.010
Soybean oil B2	Yellow	Fatty	0.9391±0.012	1.466±0.021
Rapeseed oil	Brownish yellow	Fatty	0.9110±0.011	1.468±0.011
Blend	Greenish yellow	Fatty	0.9419±0.021	1.465±0.051
p-value			0.65	0.84

**B1 and B2 indicate different brands using the oil from the seeds of the same plant.*

Table 2. Physicochemical properties of the selected oils and their blend

Oil	Saponification value (mg KOH g^{-1} oil)	Acid value (mg KOH g^{-1} oil)	Peroxide value (mEqv. of O_2 Kg^{-1} oil)
Sunflower oil *B1	206.25 ±5.82[a**]	0.442±0.009[d]	14.50±0.424[b,c]
Sunflower oil B2	184.32±5.12[b]	1.328±0.183[a]	16.50±0.707[a,b]
Corn oil B1	181.16±1.64[b'c]	0.641±0.045[b'c]	5.10±0.424[e]
Corn oil B2	186.81±3.56[b]	1.150±0.139[a]	6.60±1.979[e]
Canola oil B1	191.43±5.12[b]	0.324±0.013[c;d]	18.40±0.283[a]
Canola oil B2	185.98±4.73[b]	1.217±0.024	10.00±0.566[d]
Soybean oil B1	170.95±4.18[c]	0.756±0.041[b]	13.40±0.848[c]
Soybean oil B2	180.96±2.04[b'c]	1.136±0.020[a]	10.90±0.141[d]
Rapeseed oil	185.52±5.39	0.479±0.013[c'd]	9.80±0.001[d]
Blend	191.42±2.10[b]	1.157±0.108[a]	10.35±0.919[d]
Standard values	92 to 250	0.6	10
p-value	0.003	0.000	0.000

*B1 and B2 indicate different brands using the oil from the seeds of the same plant.
**Mean±standard deviation of three replicates. The mean values labeled with different alphabets in the same column are statistically different at 95% confidence level (p≤0.05) using Tukey's multiple range tests

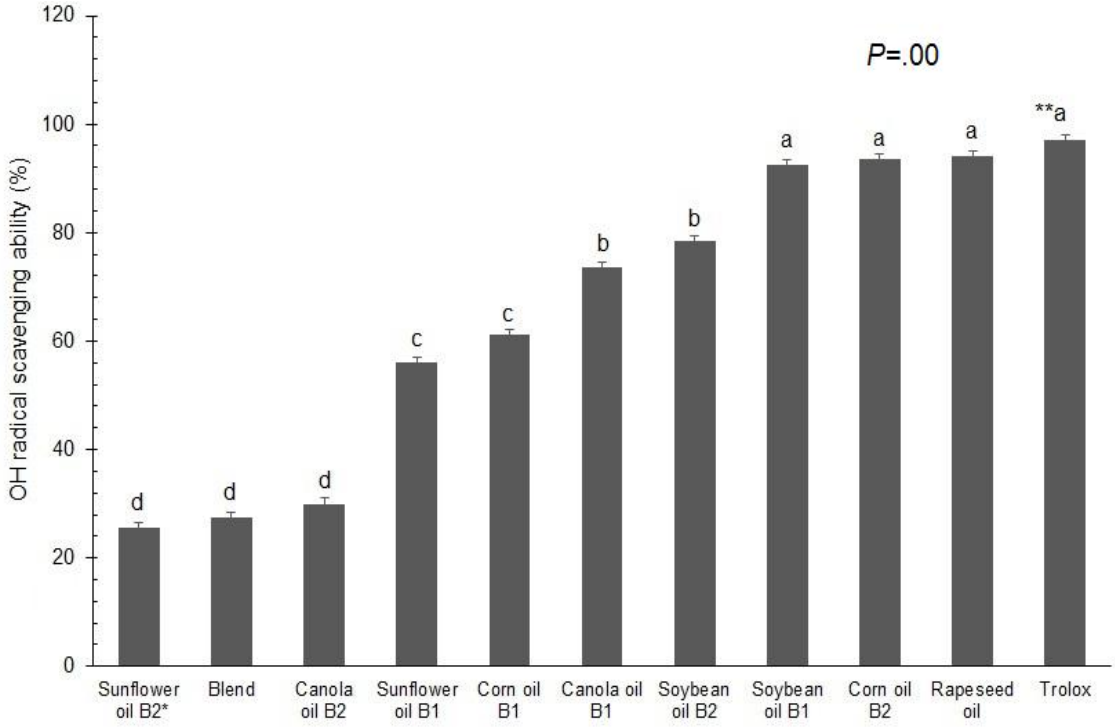

Fig. 2. Hydroxyl radical scavenging ability of oil samples of different brands
*B1 and B2 indicate different brands using the oil from the seeds of the same plant
**The error bars represent the standard deviation of three parallel replicates. The error bars labelled with different alphabets are statistically different at 95% confidence level (p≤0.05) using Tukey's multiple range tests

3.3 Screening Tests

The screening of the selected oils confirmed the presence of vitamin A in the selected oils except sunflower oil B1, corn oil B1 and canola oil B1 which were found to be deficient in vitamin A. According to the PSQCA, the oils deficient in vitamin A possess relatively low nutritional quality.

The screening test for rancidity showed that the sunflower oil B2, canola oil B1 and soybean oil

B1 showed positive signs of rancidity which may be attributed to relatively high peroxide value in these oils.

3.4 Antioxidant Potential

The antioxidant potential of the selected oils was determined in terms of OH-RSC and DPPH RSC. The results for OH-RSC and DPPH-RSC of the selected oils are presented in increasing order in Fig. 2 and Fig. 3 respectively. The OH-RSC and DPPH-RSC of the selected oils ranged from 27.5±2.121 to 97±1.01 and 21.36±3.181 to 64.97±3.783% respectively.

A statistically significant difference (*P*=.00) was observed in the free radical scavenging capacity of different oils and their blend. Rapeseed oil and corn oil B1 showed comparatively higher OH-RSC and DPPH-RSC respectively. Sunflower oil B2, canola oil B2 and blend showed comparatively lower OH-RSC and canola oil B1 showed lowest DPPH-RSC. However, the scavenging capacity of all of the selected oils against both of the free radicals was found to be lower than that of Trolox, a standard antioxidant.

The OH and DPPH radicals are the types of reactive oxygen species (ROS) and reactive nitrogen species (RNS). Both the ROS and RNS are produced in our body during the redox reaction in routine and cause oxidative damage to biomolecules if let uncontrolled. The substances which have the ability to donate electrons act as potent scavengers of these reactive species, reduce the oxidative stress and protect from oxidative damage to food materials and living system [27]. In present study, the rapeseed oil and corn oil B1 were found to be comparatively more stable towards oxidative stress due to high value of free radical scavenging capacity. The higher free radical scavenging capacity also provide an evidence that these rapeseed oil and corn oil B1 are comparatively rich in antioxidant compounds which may be helpful in preventing the oxidative damage in human. It may also be correlated with relatively lower saponification, acid and peroxide values with no signs of oxidative rancidity in both of these oils.

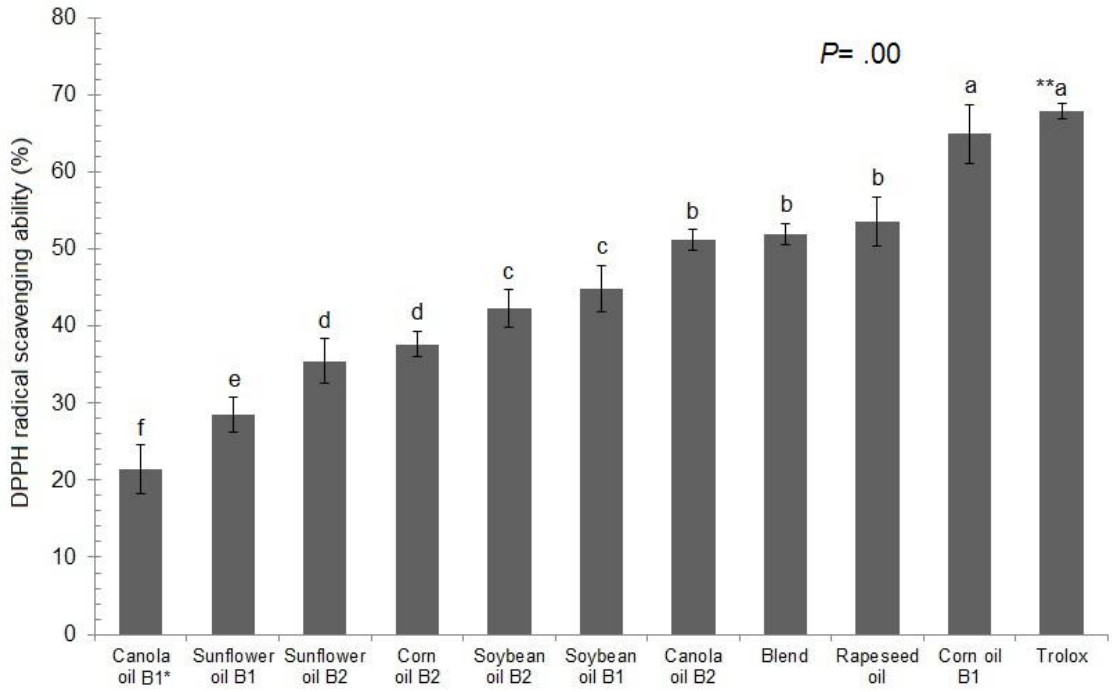

Fig. 3. DPPH radical scavenging ability of oil samples of different brands

`B1 and B2 indicate different brands using the oil from the seeds of the same plant.

***The error bars represent the standard deviation of three parallel replicates. The error bars labelled with different alphabets are statistically different at 95% confidence level (p≤0.05) using Tukey's multiple range tests*

Table 3. Screening of vitamin A and rancidity in the selected oils and the blend

Samples	Vitamin A	Rancidity
Sunflower B1*	-	-
Sunflower B2	+	+
Corn oil B1	-	-
Corn oil B2	+	-
Canola oil B1	-	+
Canola oil B2	+	-
Soybean oil B1	+	+
Soybean oil B2	+	-
Rapeseed oil	+	-
Blend	+	+

B1 and B2 indicate different brands using the oil from the seeds of the same plant

4. CONCLUSION

It is concluded that the selected cooking oils possess good physical properties. The sunflower oil B2 was found to be of low quality due to relatively high saponification, acid and peroxide value. The quality of corn oil B2, canola oil B2 and the blend was also found to be low due to high acid value. The sunflower oil B1, canola oil B1 and soybean oil B1 showed comparatively higher peroxide values with clear signs of rancidity. However, the rapeseed oil and corn oil B1 showed relatively lower saponification, acid and peroxide values with no signs of oxidative rancidity. Both of these two oils were also found to possess comparatively higher antioxidant potential in terms of free radical scavenging capacity. Therefore, the rapeseed oil and corn oil B1 were found to be the best among the selected oil due to acceptable physical, physicochemical and antioxidant properties. The study results provide valuable information to the consumers and the researchers for selection of the best quality cooking oils.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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