Investigation of Physicochemical, Spectroscopic Characteristics and the Concentration of Some Metals in Canola Oil

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Authors' contributions

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

Original Research Article

ABSTRACT

Canola oil is extracted from Rapeseed which of the family of the Brassicaceae. The oil is used in cosmetic, medicine, cooking, and soaps. In this study the chemical properties of canola oil which are acid value, percent free fatty acid, saponification value and peroxide value were determined. It has been shown 0.5035 mg/g, 0.253%, 186.26 mg/g and 1.05 mg/kg respectively. Also physical properties like density and colour was found to be 0.914 g/ml, and yellow respectively. Chemical bonds and functional group were also detected in canola oil. It shown to contain a double bond and terpenoids, by simple test, also was shown the absence of phenol functional group. The composition of canola oil was studied by IR analysis to detect the functional group like carbonyl group, C-H saturated bond and O-H group. The concentration of metal ions like Na, Fe, Zn and Cu were determined using atomic absorption spectrophotometer and was found to be 9.3885, 0.632, 0.0549, 0.116 mg/L respectively. The fatty acids in canola oil have been identified by the GC - FID, and shown to have a number of fatty acids such as oleic acid, linoleic, palmitic and other acids.

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1. INTRODUCTION

Vegetables oils and animal fats are triglyceride molecules, in which three fatty acid groups or esters attached to one glycerol molecule [1]. Fats and oils are primary water-insoluble, hydrophobic substances in the plant and animal kingdoms [2]. The advantages of vegetable oils are liquidity, ready availability, renewability, lower sulphur and aromatic content [3]. Main disadvantages are higher viscosity, lower volatility and the reactivity of unsaturated hydrocarbon chains [4].

In quality control of edible oils, many parameters such as saponification value, peroxide value, iodine value, free fatty acid content and moisture content to determine the quality of the products [5]. The major factors affecting edible oil quality are temperature, moisture, sunlight, nutrients and soil fertility [6].

Canola oil extracted from rapeseed which is a bright yellow flower of the family of the Brassicaceae, grown in European Union, Unites States, Canada, Australia, China and India. It is an important oil crop species and its cultivation has significantly increased over recent years [7]. Canola oil can be extract by different methods like pressing and solvent extraction. In pressing method the cooked canola seed flakes are pressed in a series of screw presses or expellers. This action removes part of the oil while avoiding excessive pressure and temperature. The objective of pressing is to remove as much oil as possible, usually 50-60% of the seed oil content, while maximizing the output of the expellers and producing a press cake that is ideal for solvent extraction. Since pressing alone cannot remove all of the oil from the canola seed, the press cake is usually solvent extracted to remove the remaining oil. The cake from the expellers, containing 18-20% oil [8]. Almost all commercial canola oil is then extracted using hexane solvent [9].

Canola oil contains many fatty acids. It contain 6–14% α-linolenic acid, 50–66% oleic acid which are unsaturated, and the lowest amount (< 7%) of saturated fatty acids. Also it contains tocopherols, phytosterols and Beta-carotene [10]. Canola oil has multiple uses. It used for heart health, lowers cholesterol, reduces inflammation, skin Care, increases energy levels and lowers cancer risk [11].

The content of elements and their chemical forms occur naturally in foods due to the soil where it was grown or the manufacturing process. Some of these elements are essential for a healthy, but some of them can be toxic for humans. In particular, in vegetable oils, the content of trace amount of elements affects the quality of the product. Trace elements can promote the oxidation of unsaturated bonds in lipids that gives hydrocarbons, esters, ethers, aldehydes and ketones as reaction product. These degradation reactions increase the rancidity of oils. Trace elements in vegetable oils can be determined by various techniques, such as inductively coupled plasma optic emission (ICP-OES) or mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS) and electro analytical techniques including sample preparation step. Wet or dry ashing of oil matrix is commonly used for the mineralization of the sample [12].

The aim of the work in this study is to determine the physico- chemical properties and the composition of canola oil using different methods and instruments. In this study the concentration of selected metal ions like Na, Fe, Zn and Cu were determined.

2. MATERIALS AND METHODS

2.1 Equipment

Digital analytical balance was used to weigh oil sample. Digestive furnace (Kjeldal method) was used for sample digestion. Conical flasks, beakers, pipette and volumetric flasks were used in the preparation of sample and standard solutions. Atomic absorption Spectrophotometer B13-N-232 (Agilent Technologies 200 series AA, model 240FS AA). Infra red spectrum (Nicolet 6700) Thermo scientific. The Nicolet 6700 spectrometer can be configured for multiple spectral ranges, (far-IR to UV -Vis). It is made by American thermo scientific company. Gas Chromatography with flame ionization detector (GC-2010 plus) was used for determination of fatty acids in oil sample. It was made by Japanese Shimadzu Company.

2.2 Chemicals (Reagents)

Nitric acid, sulphuric acid and hydrogen peroxide reagents were used for digestion of oil sample. Chloroform, glacial acetic acid, potassium iodide,

sodium thiosulphate, potassium hydroxide, hydrochloric acid, ethanol, and phenolphthalein for estimation of chemical properties of oil. The reagents used are Analytical Reagent grade.

2.3 Analysis of Metals

2.3.1 Determination of metals using wet digestion method

1 gram of oil sample was weighed in 50 mL conical flasks. 20 mL of a freshly prepared mixture of concentrated $HNO_3 - H_2O_2$ (2 : 1, v/v) and 3 mL of H_2SO_4 solution were added to each flask and kept for 10 min at room temperature.

The sample solutions were heated on Kjeldahl (KDN-20) digestive furnace at 250°C until a clear solution was obtained. Then, the samples were evaporated and the semidried mass was dissolved in 5 mL 0.2 M HNO_3, then filtered through Whatman number 42 filter paper, and made up to final volume of 50 mL in volumetric flasks with ultrapure water and metal contents were determined in the diluted solutions by flame atomic absorption spectroscopy [13].

2.3.2 Analysis using atomic absorption spectrophotometer

Flame atomic absorption spectrometer equipped with air/acetylene flame with deuterium lamp background correction and hollow cathode lamp for individuals metals as radiation source was used for determination of Zn, Cu, and Fe and flame photometer was used for determination of Na. Stock standard solutions containing 1000 mg/L in 2% HNO_3 of the metals Zn, Cu, Fe and Na were prepared from atomic absorption spectroscopic standard solution. The stock solutions were then used for preparation of calibration standards and spiking standards in the analysis of the samples [14].

2.4 Method for Determination of Acid Value

Five grams of oil sample was weighed in 250 mL of conical flasks and 50 mL of ethanol was added to the samples and then shaken well to dissolve sample, then 1 mL of phenolphthalein indicator was added to the sample solution. The sample solution was treated with potassium hydroxide solution until permanent pink light color appeared. The acid value was estimated using the following equation:

$$Acid\ value = \frac{56.1 \times V \times N}{W}$$

$$\%FFT = \frac{N(KOH) \times 282 \times 1000 \times Eq}{W \times 1000}$$

Where W is weight of oil, V is titre value of 0.1 N KOH, 282 is M.wt of oleic acid and 56.1 is M.wt of KOH [15].

2.5 Method for Determination of Saponification Value

Two grams of oil sample was weighed in 250 mL Erlenmeyer flasks; then 25 mL of alcoholic potassium hydroxide solution was KOH (0.1N) added into the flasks. The blank determination was conducted along with the sample.

The samples flask and the blank flask were connected with air condensers and boiled gently in the water bath, steadily until the saponification was completed, indicated by absence of oily matter and the appearance of clear solution. 1 mL of phenolphthalein indicators was added to the solution. Excess potassium hydroxide was titrated with 0.5 N hydrochloric acid until cloudy solution was formed The saponification value was estimated using the following equation:

$$saponification\ value = \frac{56.1 \times (b - a) \times N}{W}$$

Where w is weight of sample that equals 2 grams, b is blank titre value, a is sample titre value, and N is 0.5 normality of HCl [16].

2.6 Method for Determination of Peroxide Value

Five grams of oil sample was weighed in 250 mL of conical flask; then, 30 mL of acetic acid and chloroform solvent mixture (3 : 2) was added to oil sample and swirled to dissolve. Then, 0.5 mL of potassium iodide solution was added to the solution. The solution was kept for 1 min in dark room with occasional shaking and titrate liberated iodine in 0.01 N sodium thiosulphate solution until vigorously shaking yellow color was gone and after that 1 mL of starch solution indicator was added and we continued titration by vigorous shaking to release all I_2 from CH_3Cl layer until blue color disappeared. The peroxide value was estimated using the following equation:

$$peroxide\ value = \frac{V \times M \times 100}{W}$$

where V is volume of sodium thiosulphate, N is normality used for titre, W and is weight of the sample [17].

2.7 Determination of Density

Density of oil sample was measured by an R.D bottle with a capacity of 10 mL.

$$\text{Density} = {m}/{v} \text{ [gcm}^{-3}\text{]}$$

Where: m = mass of oil, v = volume of oil [18].

2.8 Test for Double Bond

Small quantity of canola oil was mixed with drops of potassium permanganate ($KMnO_4$). A positive test disappearance of the purple ($KMnO_4$) and the appearance of (MnO_2) as a brown precipitate.

2.9 Test for Phenol Functional Group

Small quantity of canola oil was mixed with water and heated on water bath. the mixture was filtered and ferric chloride ($FeCl_3$) added to the filtrate. A dark green or blue-black solution indicates the presence of tannins.

2.10 Test for Terpenoids

0.2 g of the canola oil of the whole plant sample was mixed with 2 ml of chloroform ($CHCl_3$) and 3 ml of concentrate sulphuric acid was carefully added to form a layer. A reddish brown Formed to indicate positive result for the presence of terpenoids.

3. RESULTS AND DISCUSSION

3.1 Analysis of Metals Using FAAS

The concentration of some selected metals in canola oil sample was determined by using flame atomic absorption spectroscopy (FAAS) techniques using calibration curve.

The concentration of metals like Na, Cu, Fe and Zn was detected as shown in Table 1, and were found in the range of acceptable value, according to WHO (Table 2).

3.2 Physico-Chemical Properties of Canola Oil

Some of physico-chemical properties such as acid value, peroxide value, saponification value, density and color were determined in the selected sample and compared with the codex standard [19] which is presented in Table 3, reported in terms of mean plus standard deviation.

3.2.1 Acid value

Oils and fats contain a lot or a small amount of free fatty acids depending on storage conditions and technical processes, where glycerides break down into their products (including free fatty acids) by enzymes, air or bacteria. The acid value must be not more than 0.6 mg/g from WHO recommendation and the obtained result for canola oil is 0.5035 mg/g which is below the permissible limit.

Table 1. Concentration of metal in canola oil

Metal	Fe	Cu	Zn	Na
Conc. (ppm)	0.632	0.116	0.0549	9.3885

Table 2. Standard value of metal concentration according to WHO

Metal	Na	Fe	Cu	Zn
Conc. (ppm)	≤ 175	0.1-2.0	0.1 – 4	0.10 – 5

Table 3. Physiochemical properties of canola oil

Property	Acid value mg/g	Free fatty acid %	Peroxide value mg/kg	Saponification value mg/g	Density g/cm^3	Color
Result	0.5035±0.08	0.253±0.04	2.1 ± 1.48	186.26 ± 2.4	0.9147	Yellow
Codex stan.	0.6	0.3	-	182-193	0.910-0.920	Yellow

Table 4. Standard values for oils according to WHO

Property	Acid value mg/g	Peroxide value mg/kg	Saponification value mg/g	Density g/cm^3
Value	Not more than 0.6	Not more than 10	186 - 195	0.919 - 0.925

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3.2.2 The peroxide value

The peroxide content (PV), measured in milliequivalents of active oxygen per kilogram, determines the initial oxidation of an oil. The rate of peroxidation of the oil is primary arising because of the oxidation process, high temperature and visibility to light. Contact with metal surfaces can also cause faster oxidation of the oil.

The lower the value the longer the oil will retain the shelf life and will delay the possibility of rancidity, while high peroxide value usually indicates poor processing, and that the quality of the oil is low. The value of peroxide for valid canola oil is must be less than 10 mq/kg. The obtained result was 2.1 mg/kg.

3.2.3 The saponification value

The SV is the number of potassium hydroxide milligrams needed to produce fat, oil or wax in one gram of the sample. The greater the molecular weight (the longer the carbon chain), the smaller the number of fatty acids is liberated per gram of fat hydrolyzed and therefore, the smaller the saponification number and vice versa. The composition of canola oil varies with the cultivar, altitude, time of harvest and extraction process. The value of saponification value for canola oil was 186.26 mg/g, which was in the permissible range.

3.3 The Test for Double Bond

The color turned into brown deposit. This indicate the presence of a binary bond and which was broken down and converted to single bond by adding potassium permanganate to the oil.

3.4 The Test of Phenol Functional Group

After making test by adding iron chloride, there is no color change which indicates the absence of phenol group in canola oil.

3.5 The Test of Terpenoids

After the addition of chloroform and sulphuric acid, there is color change which indicates the existence of terpenoids in canola oil.

3.6 Infra Red Analysis

The composition of canola oil was studied by IR analysis to detect the functional group like carbonyl group, C-H saturated bond and O-H group. The vibrations of bonds were shown in Table 5.

3.7 GC-FID Analysis

The fatty acids in canola oil were determined using gas chromatography- flame ionization detector (GC - FID). FID typically used a Hydrogen/Air, and Helium gas flame into which the sample was passed to oxidize organic molecules and produces electrically charged particles (ions). The ions were collected and produced an electrical signal which was then measured. The percent of fatty acids found in canola oil were compared with another sample [20] which are shown in Table 6.
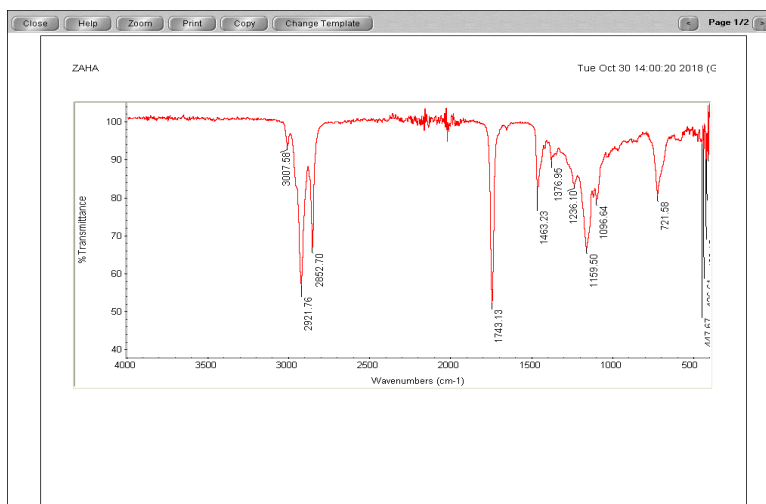

Fig. 1. IR spectrum of functional groups in canola oil

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Table 5. IR analysis

Frequency(cm^{-1})	Functional group assignment
3007.58	Hydrocarbons (C-H Absorption) Alcohol
2921 and 2852	Asymmetrical and symmetrical stretching vibration of methylene (CH$_3$)
1743.12	Ester carbonyl functional group of the triglyceride
1463.23 and 1376.95	Bending vibration of the CH$_2$ and CH$_3$aliphatic group
1236.10 and 1159.50	C -O Stretching
1096.64	Stretching vibration of the C-O ester group
722	Overlapping of the methylene (CH$_2$) rocking vibration of cis-disubstituted olefin

Table 6. GC-FID analysis

Peak	Cmpd.	Cmpd. name	w/w%	w/w% (another study)	Ret. time	Area	Height
1	C16:0	plamitic acid	4.2477	4.06	9.884	169019	65349
2	C16:1	plamitoleic acid	0.2121	0.23	10.554	8440	3106
3	C18:0	stearic acid	1.8161	1.54	12.962	72266	19570
4	C18:1	Oleic acid	62.6693	62.29	13.839	2493687	456414
5	C19:0	Nonadecanoic acid	0.1702	-	14.701	6771	1983
6	C18:2	Linoleic acid	20.7676	20.65	15.112	826367	206739
7	C18:3	Linolenic acid	7.9409	8.71	16.808	315979	84869
8	C20:0	Arachidic acid	0.6065	0.87	17.001	24123	6627
9	C20:1	Eicosenoic acid	1.2312	1.09	17.981	48993	12942
10	C22:0	Behenic acid	0.3384	0.27	21.932	13466	3213
Total			100.0000			3979120	3213
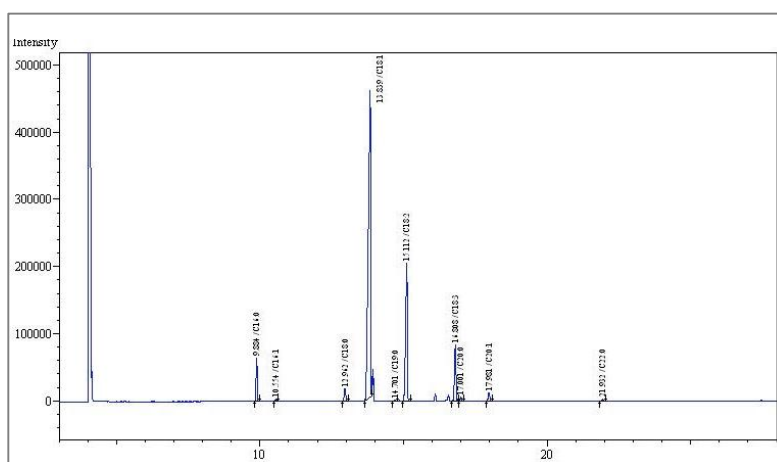
Fig. 2. GC-FID analysis of fatty acid in canola oil

4. CONCLUSION

The work was intended to study the physico - chemical properties and spectrophotometric analysis of canola oil. The lower acid value is an advantage that canola oil cannot develop off (rancidity) flavour during storage and enables the direct use of the oil without further neutralization. The study shown the presence of double bond, terpenoids and absence of phenol group in canola oil. The composition of canola oil was investigated using IR analysis and GC-FID spectrophotometer, which confirmed the presence of many function group and fatty acids.

An analysis was performed to determine the concentration of some selected metals and was found in the permissible range.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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