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Phytochemical Screening of *Coriandrum sativum* Extract and Influence in Chemical Properties of Sunflower Oil

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Abstract: Oxidation is a chemical reaction that can produce free radicals, leading to chain reactions that may damage cells. An antioxidant is a molecule that inhibits the oxidation of other molecules. This study was designed to determine the effect of coriander extract on the chemical properties of fresh and storage sunflower oil. Coriander oil was extracted by water steam distillation process, then GC-MS was used to determine the chemical profile of coriander oil which revealed that the coriander seeds oil contains 24 compounds were; Heptanal, α-Thujene, α-Pinene, Camphene, β-Phellandrene, β-Pinane, p-Cymene, γ-Terpinene, 1-Octanol, Linalool, Camphor, Trimethy-cyclohexene carboxaldehyde, Decanal, Cuminaldehyde, *cis*-2-Decenal, Thymol, 1-Propanol, 2-Methyl-1-phenyl, *trans*-2-Dodecenal, Tetradecanoic acid, Phthalic acid, Dibutyl phthalate, Tetradecanoic acid, Diisobutyl phthalate and Palmitic acid. The chemical properties (peroxide, acid and saponification value) of sunflower oil were examined for both fresh and storage sample. The storage sample was tested during five interval period along 75 day. The coriander oil was appeared significant clear effect ($p < 0.05$) on chemical properties of sunflower oil, so the study revealed that the coriander oil had clear influence on the chemical properties of the sunflower oil and mainly on the reused edible oil sample. The study could be attributed that to the coriander extract is richly oil in antioxidants such as monoterpens and sesquiterpenes which serves to decline the high autoxidation of sunflower oil.

Keywords: Coriander, Peroxide Value, Saponification

1. Introduction

Coriandrum Sativum (Coriander) is an annual apiaceous herb, which grows in Mediterranean countries. The fun fact about coriander is that, ancient reasoning attributed anything with such a pronounced and unpleasant odor to possess powerful curative or preventative attributes. Coriander seeds have been found in Egyptian tombs dating to the 21st dynasty [1]. India is the biggest producer, consumer and exporter of coriander in the world with an annual production of around three lakh tonnes. It is an annual, herbaceous plant which originated from the Mediterranean and Middle Eastern regions and known as medicinal plants. It contains an essential oil (0.03 to 2.6%) [2].

Coriander is widely used in food and pharmaceutical industries. All parts of plant are edible, fresh leaves can be used for garnishing and are common ingredient in many foods like chutneys and salads. The green herb is also employed for the preparation of either steam-distilled essential oil or the solvent extracted oleoresin [3]. In traditional medicine, seeds are used in the treatment of gastrointestinal problems, rheumatism and pain joints [4]. Recent studies have also demonstrated a hypoglycemic action and effects on carbohydrate metabolism. It has also been reported the antimicrobial effect of coriander leaves and seeds against several microorganisms. Furthermore in food industry, leaves and seeds are employed as condiment, being used to flavour various commercial foods, as liqueurs, teas, meat products and pickles [5]. The coriander oil can be encapsulated in alginates, chitosan etc. so as to enable isolation, protection, transport and release of its active components like vitamins, flavours, peptides, minerals, fatty acids, polyunsaturated fatty acids, antioxidants, enzymes and living cells [6].

The phytochemical screening of plant showed the presence of tannins, terpenoids, reducing sugars, alkaloids, phenolics, flavonoids, fatty acids, sterols and glycosides. The most important constituents of coriander fruits were the essential

oil and fatty oil. The essential oil content of dried coriander fruits varies between 0.03 and 2.6%, while the fatty oil content varies between 9.9 and 27.7%. The variations in the oil constituents of coriander leaves and seeds could be attributed to the variations in the cultivar and not due to geographic divergence and ecological conditions [7]. The analysis of the essential oil conducted by gas chromatography-mass spectroscopy, revealed 33 components, representing 99.99% of the total oil from the seeds of coriander. The major components were linalool (55.09%), α-pinene (7.49%), 2,6-octadien-1-ol, 3,7-dimethyl-, acetate, (E)- (5.70%), geraniol (4.83%), 3-cyclohexene-1-methanol, α,α,4-trimethyl- (4.72%), hexadecanoic acid (2.65%), tetradecanoic acid (2.49%), 2-α-pinene (2.39%), citronellyl acetate (1.77%), and undecanal (1.29%) [8]. Investigation of chemical composition of coriander seeds showed that linalool was the most abundant compound in all samples, followed by camphor, methyl chavicol, (+)-limonene, eucalyptol, eugenol, geraniol, γ-terpinene and α-terpineol. Furthermore, antioxidant activity of obtained extracts was determined using two different assays. Obtained results showed that observed extracts exhibit higher activity against lipid peroxidation, than against DPPH radical with the lowest inhibitory concentrations of 0.101 mg/mL and 2.364 mg/mL, respectively [9].

Edible oil is a triglyceride extracted from a plant. The term “edible oil " can be narrowly defined as referring only to substances that are liquid at room temperature, or broadly defined without regard to a substance's state of matter at a given temperature. For this reason edible oil that are solid at room temperature are sometimes called edible fats. Edible oils are composed of triglycerides, as contrasted with waxes which lack glycerin in their structure. Although many plant parts may yield oil, in commercial practice, oil is extracted primarily from seeds [10]. Plant and animal or synthetic fat used in frying, baking, and other types of edible. It is also used in food preparation and flavoring not involving heat, such as salad dressings and bread dips, and in this sense might be more accurately termed edible oil. There are a wide variety of cooking oils from plant sources such as olive oil, palm oil, soybean oil, canola oil, corn oil, peanut oil and other vegetable oils, as well as animal-based oils like butter and lard. Oil can be flavored with aromatic foodstuffs such as herbs, chillies or garlic [11].

Edible oil is oxidized during processing and storage via autoxidation and photosensitized oxidation, in which triplet oxygen ($3O_2$) and singlet oxygen ($1O_2$) react with the oil, respectively. Lipid hydroperoxides formed by three moles of oxygen are conjugated dienes, where one mole of oxygen produces both conjugated and non-conjugated dienes. Autoxidation of oil is accelerated by the presence of free fatty acids, mono- and diacylglycerols, metals such as iron, and thermally oxidized compounds [12].

Exposure to oxygen and sunlight are the two main factors in the oxidation of food, so food is preserved by keeping in the dark and sealing it in containers or even coating it in wax, as with cucumbers. However, as oxygen is also important for plant respiration, storing plant materials in anaerobic conditions produces unpleasant flavors and unappealing colors. Consequently, packaging of fresh fruits and vegetables contains an 8% oxygen atmosphere. Antioxidants are an especially important class of preservatives as, unlike bacterial or fungal spoilage, oxidation reactions still occur relatively rapidly in frozen or refrigerated food [13].

The peroxide value is defined as the amount of peroxide oxygen milliequivalents per 1 kilogram of fat or oil. The double bonds found in fats and oils play a role in autoxidation. Oils with a high degree of unsaturation are most susceptible to autoxidation. The best test for autoxidation (oxidative rancidity) is determination of the peroxide value. Peroxides are intermediates in the autoxidation reaction. Peroxide values of fresh oils are less than 10 milliequivalents /kg; when the peroxide value is between 30 and 40 milliequivalents/kg, a rancid taste is noticeable [14]. The number of mg of potassium hydroxide required to saponify 1 gram of oil/fat. The oil sample is saponified by refluxing with a known excess of alcoholic potassium hydroxide solution. The saponification value is an index of mean molecular weight of the fatty acids of glycerides comprising a fat. Lower the saponification value, larger the molecular weight of fatty acids in the glycerides and vice-versa. The alkali required for saponification is determined by titration of the excess potassium hydroxide with standard hydrochloric acid [15].

Antioxidants are used as food additives to help guard against food deterioration. An antioxidant is a molecule that inhibits the oxidation of other molecules. Oxidation is a chemical reaction that can produce free radicals, leading to chain reactions that may damage cells. Antioxidants such as thiols or ascorbic acid (vitamin C) terminate these chain reactions. The term "antioxidant" is mainly used for two different groups of substances: industrial chemicals which are added to products to prevent oxidation, and natural chemicals found in foods and body tissue which are said to have beneficial health effects [16]. By definition, the oxidative stability of oil is a measure of the length of time taken for oxidative deterioration to commence. On a general level, the rates of reactions in auto oxidation schemes are dependent on the hydrocarbon structure, heteroatom concentration heteroatom speciation, oxygen concentration, and temperature [17]. If untreated, oils from vegetable origin oxidize during use and polymerize to a plastic like consistency [18]. Even when they are not subjected to the intense conditions of industrial applications, fats and oils are liable to rancidity. This happens more so in fats that contain unsaturated fatty acid radicals [19]. To balance the oxidative state, plants and animals maintain complex systems of overlapping antioxidants, such as glutathione and enzymes (e.g., catalase and superoxide dismutase). Antioxidant dietary supplements do not improve health nor are they effective in preventing diseases as shown by randomized clinical trials including supplements of beta-carotene, vitamin A, and vitamin E singly or in different combinations having no effect on mortality rate [20].

2. Objectives of the Study

This study searches to achieve these aims:

1. To extract the coriander oil.
2. To determine the chemical properties of coriander oil.
3. To detect the effect of coriander extract on the chemical properties of fresh and storage sunflower oil.

3. Methods

3.1. Extraction of Coriander Oil

Coriander oil was extracted by steam distillation and water process. Mature coriander seeds were put into distillation instrument over water, then the water was heated and the steam passed through the coriander seeds and vaporized the volatile compounds. The vapors were flowed through a coil, where they were condensed back to liquid, which then was collected in the receiving vessel. At the end of the distillation process coriander oil was separated from water depending on the difference in their density by using laboratory separating funnel. The oil of coriander was collected and kept at suitable temperature in dark pure bottle and had been ready for chemical profile analysis and to determine the chemical and physical tests.

3.2. Determination of Coriander oil Components

Coriander oil was analyzed by using a gas chromatography mass spectrometry (GC- MS, QP 2010 plus), equipped with selective detector mass spectrometry. The identification of oil constituents was carried out by comparing retention times with those of authentic reference compounds, or peak matching library research using the standard mass library.

3.3. Determination of Chemical Properties

3.3.1. Determination of Peroxide Value (PV)

Principle:

PV is a redox titrimetric determination. The assumption is made that the compounds reacting under the condition of the test are peroxides or similar product of lipid oxidation. Addition of excess potassium iodide reacts with the peroxide, iodine is produce. Through titration process, iodide reacts with standardized sodium thiosulfate using a starch as indicator.

$$2I^- + \text{starch } (\textit{blue}) + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 + \text{starch } (\textit{colorless})$$

Procedure:

5g of sample were weighed into a 250 ml stopper conical flask, 30 ml acetic acid and chloroform solvent mixture in the ratio of 3:2 were added and swirled until was dissolved, then 0.5 ml saturated potassium iodide solution was added with a Mohr pipette. The mixture solution was stand for 1min in dark with occasional shaking, after that about 30 ml of distilled water were added and also about 0.5 ml of starch solution as indicator and then the reaction was initiated and continued with shaking vigorously until all iodine (I_2) was released from chloroform ($CHCl_3$) layer. The liberated iodine was slowly titrated with 0.1 N sodium thiosulphate solution or (0.001 mol/l) $Na_2S_2O_3$, with vigorous shaking until the colour was a disappeared.

Calculation:

$$\text{Peroxide value} = \frac{\text{titer} \times \text{N} \times 100}{\text{Sample weight}}$$

Where,

Titre: ml of sodium thiosulphate used (blank corrected)

N: normality of sodium thiosulphate solution.

3.3.2. Determination of acid Value

Principle:

The acid value is determined by directly titrating the oil in an alcoholic medium against standard potassium hydroxide solution. The value is a measure of the amount of fatty acids which have been liberated by hydrolysis from the glycerides due to the action of moisture and temperature.

$$\text{RCOOH} + \text{KOH} \xrightarrow[\text{Heat}]{\text{Light}} \text{RCOOK} + H_2O$$

Procedure:

A accurately appropriate amount of the cooled oil sample was weighed in a 250 ml conical flask, 50 ml of freshly neutralized hot ethyl alcohol was added and one ml of phenolphthalein indicator solution. The mixture was boiled for five minutes and titrated against standard alkali solution 0.100N or 0.001M with vigorously shaking during the titration.

Calculation:

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

Where,

V: volume in ml of standard potassium hydroxide used.

N: normality of the potassium hydroxide solution.

W: weight in g of the sample.

3.3.3. Determination of Saponification Value

Principle:

The oil sample is saponify by refluxing with a known excess of alcoholic potassium hydroxide solution. The alkali required for saponification is determined by titration of the excess potassium hydroxide with standard hydrochloric acid.

Procedure:

A portion (3g) of the sample was measured into a flask and 25ml of alcoholic potassium hydroxide solution was added to it. A reflux condenser was attached to the flask and the solution heated for one hour with occasional shaking. A 3 drops of phenolphthalein solution was added and titrated with 0.5m HCl. A blank was carried out with water and recorded.

Calculation:

$$\text{Saponification Value} = \frac{(\text{b} - \text{a}) \times 28.05}{\text{w}}$$

Where,

b: volume in ml of standard hydrochloric acid required for the blank.

a: volume in ml of standard hydrochloric acid required for the sample.

w: weight in gm of the oil/fat taken for the test.

3.4. Statistical Analysis

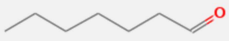
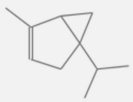
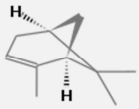
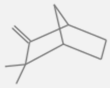
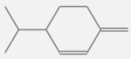
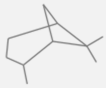
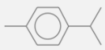
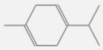
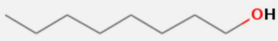
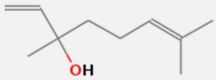
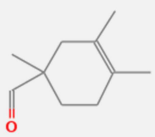
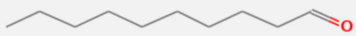
Data was collected and entered into the statistical analysis program (SPSS) using the windows computer system (IBM). The P value was considered significant at < 0.05 and the maximum confidence was 95%.

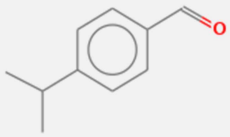
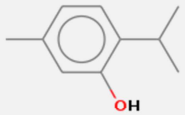
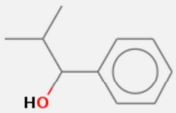
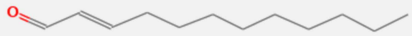
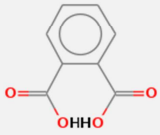
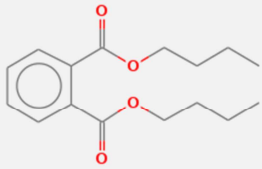
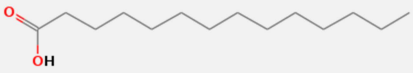
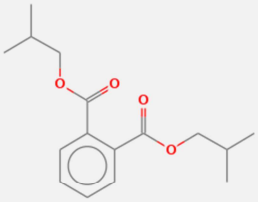
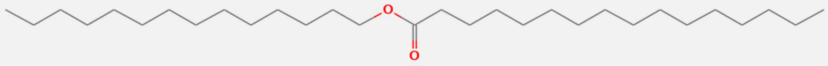
4. Results and Discussion

4.1. GC-MS Result

The coriander oil obtained by steam distillation which was colorless to pale yellow liquid was analyzed by GC-MS. The main constituents of coriander oil were; hydrocarbons, monoterpene, aldehydes, alcohols, phenols, acids and esters, Table 1, represented that.

Table 1. *Chemical components of coriander extract.*

Constituent	Formula	Structure
Heptanal	$C_7H_{14}O$	
α-Thujene	$C_{10}H_{16}$	
(R)-α-pinene	$C_{10}H_{16}$	
Camphene	$C_{10}H_{16}$	
β-Phellandrene	$C_{10}H_{16}$	
Pinane	$C_{10}H_{18}$	
p-Cymene	$C_{10}H_{14}$	
γ-Terpinene	$C_{10}H_{16}$	
1-Octanol	$C_8H_{18}O$	
Linalool	$C_{10}H_{18}O$	
d-camphor	$C_{10}H_{16}O$	
Trimethyl-3-cyclohexene-1-carboxaldehyde	$C_{10}H_{16}O$	
Decanal	$C_{10}H_{20}O$	

Constituent	Formula	Structure
Cuminaldehyde	$C_{10}H_{12}O$	
2-Decenal	$C_{10}H_{18}O$	
Thymol	$C_{10}H_{14}O$	
1-Propanol, 2-methyl-1-phenyl	$C_{10}H_{14}O$	
trans-2-dodecenal	$C_{12}H_{22}O$	
Tetradecanoic acid	$C_{14}H_{28}O_2$	
Phthalic acid	$C_8H_6O_4$	
Dibutyl phthalate	$C_{16}H_{22}O_4$	
Tetradecanoic acid	$C_{14}H_{28}O_2$	
Diisobutyl phthalate	$C_{16}H_{22}O_4$	
Palmitic acid	$C_{30}H_{60}O_2$	

4.2. Chemical Properties of Coriander Oil

The chemical properties peroxide value (PV), acid value (AV) and saponification value (SV) of extracted oil and sunflower oil were evaluated, table 2 show that.

Table 2. *Chemical properties of sunflower and coriander oil.*

Oil type	PV	AV	SV
Sunflower oil	2.82	0.93	184.60
Coriander oil	0.42	2.84	187.28

4.3. Effect of Coriander Oil on the Chemical Properties

The effect of coriander oil on the chemical properties (peroxide, acid and saponification value) of sunflower oil was determined by studied the fresh and storage samples. Two pure and fresh sunflower oil samples were prepared one of them was tested at once while the other was storage to 75 day.

4.3.1. Peroxide Value

Effect of coriander extract on the primary oxidation of

sunflower oil was measured by determined the peroxide value. The peroxide value was investigated at the beginning, during (five intervals) and at the end of storage, table 3 illustrates that.

Table 3. *Peroxide value of pure and storage sample during storage period.*

Storage period	*Pure Sunflower oil*	*Mixture oil* Sample + 0.5 ml
Before storage	2.82	2.48
After 1st s.p.	4.96	4.13
After 2nd s.p.	6.82	4.80
After 3rd s.p.	8.53	5.20
After 4th s.p.	10.05	6.20
After 5th s.p.	10.76	8.26
P. value	< 0.05	< 0.05

s.p.= storage period

Peroxide value of sunflower oil had been significant increasing ($P<0.05$) with storage periods from 2.82 at the beginning of storage to 10.76 at the end of storage which indicated the occurrence of oxidation process as a result of storage. Sunflower oil is softer oil and more susceptible to oxidation because it contains double bond of unsaturated fatty acids that became aldehyde, ketones and peroxides, and when peroxides concentration reached a certain level, complex chemical changes occurred and volatile oil products were formed. After addition of coriander oil (0.5ml) of coriander oil was followed by clear decrease, this result could be explained due to that the coriander oil is good source of high antioxidant activity compounds such as monoterpene, alcohols and phenols which acts as potential antioxidants.

4.3.2. Acid Value

Acid value is a very important parameter for evaluating the quality of oils, as it represents the free content of fatty acids due to enzymatic activity. The acid value of two samples (fresh and storage) was investigated according to the following table.

Table 4. *Acid value pure and mixture sample during storage period.*

Storage period	Acid value *Pure SunflowerOil*	*Mixture oil* Sample + 0.5 ml
Before storage	0.93	0.15
After 1st s.p.	0.45	0.31
After 2nd s.p.	0.59	0.38
After 3rd s.p.	0.81	0.41
After 4th s.p.	1.09	0.49
After 5th s.p.	1.57	0.60
P. value	< 0.05	< 0.05

This parameter can be used to verify the level of oxidizing degradation of oil from enzymatic or chemical oxidation. Acid value depends on the carboxyl group in the fat. In general our study was found that the acid value was increase with storage period from (0.93) at the beginning to (1.57) at the end of storage period for pure sample, and from 0.15 to 0.60 for mixture sample. This may be attributed to the storage effect during which the oxidation process was occurred in sunflower oil result in increasing of free fatty as well as acid value. After addition of coriander oil, free fatty acids were reacted with alcoholic and phenolic compounds in coriander oil to esters formation that may be decline free fatty acids and so explain the clear decrease in acid value.

4.3.3. Saponification Value

Our study showed that the saponification value of pure sunflower oil sample was 184.00 and after addition of 0.5ml coriander oil the saponification value became 193.68 at the storage beginning. These values revealed that the coriander oil act to increase the saponification value of pure and fresh sample. But in contrast the addition was decline the saponification value of storage sample from 229.93 to 200.79 at storage end. Table 5 represents that.

Table 5. *Effect of coriander oil on saponification value of sunflower oil.*

Storage period	*Sample of Sunflower Oil*	*Mixture oil* Sample +0.5 ml
Before storage	184.00	193.68
After 1st s.p.	188.98	194.00
After 2nd s.p.	199.17	196.36
After 3rd s.p.	217.25	197.37
After 4th s.p.	220.73	210.71
After 5th s.p.	229.93	200.79
P. value	< 0.05	< 0.05

In general there was clear increasing when compared between beginning and end of storage values. This might be explained due to the fact that coriander oil components as alcohols, phenols and acids were reacted with carboxylic and hydroxyl compounds in edible oil respectively which increase the triacylglycerol and so the saponification value. On the other hand the free fatty acids of coriander oil may have lower molecular weight than free fatty acids of sunflower oil.

5. Conclusion

Coriander oil was extracted by water steam distillation process then GC-MS was used to determine the chemical profile of coriander oil contains 24 compounds. Chemical properties of sunflower oil were studied, before and after addition of Coriander oil at the beginning and during of storage periods every 15 days for 75 days. The study found that coriander oil had clear impact on the chemical properties of the edible oil (Sunflower oil), and also had high effect on the reused oil sample. Coriander extract has many organic compounds such as terpenoids, alcohols and phenols which were act as a good antioxidant source so it may able to decrease and decline the oil rancidity and oxidation.

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