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Comparative study of physicochemical properties and antioxidant analysis on refined and unrefined edible oils

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Abstract

Oils extracted from plants have been used since ancient times.Vegetable oils play an important role in South Indian nutrition. The physicochemical properties of oil as value parameter are very important in evaluating the suitable uses of cooking oil. The oils included in the study were refined (coconut, groundnut, and gingely) as well as unrefined (coconut, groundnut, and gingely) oils. The results of physicochemical properties of crude and refined oils such as coconut oil, groundnut oil, gingely oil revealed that the acid value, peroxide value, saponification value, moisture content of the refined oil were lesser when compared to that of unrefined oil. Whereas the iodine value was significantly higher in refined oil compared to that of unrefined oil. The results of DPPH antioxidant assay showed that there was an increased antioxidant activity in refined groundnut oil when compared to that of other oils. The results show that refined oil is suitable for cooking purpose than unrefined oil.

Keywords: coconut oil, groundnut oil, gingely oil, acid value, peroxide value, saponification value, DPPH

1. Introduction

Edible seed oils have been extracted and used as food ingredients since ancient times. The nutritive and calorific values of seeds make them good sources of edible oils and fats diet [1]. Vegetable oils are derived from plant sources like soya beans, groundnut, corn, oil palm, sesame, coconut, etc. The term "vegetable oil" can be narrowly defined as referring only to substances that are liquid at room temperature [2]. Vegetable oils are the main source of dietary fat in India. The country has a wide range of sources of edible oils and approximately 2/3rd of the total supply of vegetable oil is met through groundnut oil, mustard oil and rapeseed oil.

The quality and stability of edible oil are the main factors that influence its acceptability and market value [3]. During processing or storage of oils, fatty acids are oxidised first to hydroperoxides which are non-volatile, odourless substances. They can easily degrade to secondary oxidation products like epoxides, saturated and non-saturated aldehydes, ketones, acids, etc., that are responsible for the rancid taste and development of unpleasant flavours. Therefore, the degree of oxidation and the potential for deterioration are important quality parameters of edible oils [4].

Coconut oil is derived from copra, which is the dried kernel or 'meat' of coconuts. The coconut palm is the species *Cocos nucifera*, which grows well in the humid regions a few degrees' latitude either side of the equator. Copra has the highest oil content of all oil-bearing crops, with an oil content of 65–68% and moisture at 4–7%. Which are easily digestible and easily absorbed into the body through the portal vein and produce energy [5].

Groundnut oil is expressed from the seed of *Arachis hypogaea* L., commonly known as groundnut, peanut, or earth nut because the seeds develop underground. Groundnut oil is a vegetable oil which contains only a small proportion of non-glyceride constituents. Although a range of 36–56% has been reported for oil content, groundnuts commonly contain 40–50% oil [6].

Sesame is also known as gingelly and tila or snehphala in Ayurveda. Sesame (*SesamumindicumL.*) is an ancient oil yielding crop and popularly known as "Queen of Oilseeds". The Sesame oil which has been traditionally used for cooking and as a flavour additive in food products of Asian and Western countries [7]. Oil is used for both dietary and therapeutic applications. Sesame oil is mostly composed of triglycerides of the singly unsaturated oleic acid (40%) and the doubly unsaturated linoleic acid (45%), besides approximately 10% saturated fats.

The major characteristics usually included in National and International standards and trading specifications and used for quality control in laboratories are as follows. Those for crude oils include the free fatty acids (FFA), iodine value (IV), saponification value (SV) refractive index (RI), specific gravity (SG), unsaponifiable matter (US), and moisture plus impurities (M&I). These are intended to give a quick impression of the authenticity of the oil and the likely losses in refining. For refined oils, the values also usually include the colour, peroxide value (PV), slip melting point (SMP) and solid fat content (SFC), if appropriate. These are indications of quality and behavior in use.

The aim of this study was to compare the quality and oxidative damage in refined and unrefined edible oils and to provide knowledge which could contribute to the commercial utilization of edible oils.

2. Materials and Methods

2.1 Samples

Coconut oil, Groundnut oil, and gingelyoil (refined and unrefined) was obtained from thelocal market in kanchipuram, Tamil Nadu, India. DPPH was obtained from Sigma. All of the reagents andsolvents used were of analytical reagent grade.

2.2 Moisture content

10g of oil has been thoroughly mixed by stirring. Loosen the lid of the dish and heat in an oven at 105℃ for 20 minutes. Remove the dish from the oven and close the lid then weigh the dish containing oil then the dish is again placed in oven for 20 minutes. This is repeated for three times until change in weight between two successive observations does not exceed 1mg [7].

Moisture and volatile matter=W1×100 / W

Where,
W1= Loss in gm of the material on drying
W= Weight in gm of the material taken for test

2.3 Saponification value (SV)

Oil sample (2.0 g) was accurately weighed into a conical flask and 25 ml of 0.5 N alcoholic KOH were added. A blank was also prepared by placing 25 ml of alcoholic KOH in a similar flask. Reflux condensers were fitted to both flasks and the contents were heated in a water bath for one hour, swirling the flask from time to time. The flasks were then allowed to cool a little and the condensers washed down with a little distilled water. The excess KOH was titrated with 0.46 M HCl acid using phenolphthalein indicator [7]. The saponification value was calculated using the following equation.

Saponification value = (b-a) × F × 28.05 /Weight of sample.

Where b = titer value of blank (ml), a = titer value of sample (ml), F = factor of 0.46 M HCl = 1 (in this case) and 28.05 = mg of KOH equivalent to 1 ml of 0.46 M HCl.

2.4 Acid value (AV)

Ethanol was boiled on a water bath for a few minutes to removedissolved gases, and neutralized by adding a few drops of phenolphthalein and about 10 ml 0.1M potassium hydroxide (KOH) until a pale pink colour was obtained. Oil sample (6.0 g) was weighed into a conical flask and 50 ml of hot previously neutralized alcohol was added. The mixture was later boiled on a water bath. The hot mixture was then titrated with 0.1N potassium hydroxide (KOH) solution until the pink colour (stable for few minutes) returned [7].

The acid value (AV) was calculated from the following expressions:

Acid value =Titer value (ml)×N×56.1 / Weight of sample

Where N = normality of KOH = 0.1M (in this case), 282 = molar mass of oleic acid and 56.1 = molar mass of KOH.

2.5 Iodine value (IV)

Oil sample (0.250 g) was weighed into a quick-fit conical flask and then dissolved with 10 ml CHCl3 and 25 ml Hanus reagent. The flask and its content were placed in the dark for about 30 min with occasional shaking. 10 ml of 15% KI solution was later added with thorough shaking and the solution on the side of the flask and the stopper was washed down with 100 ml of distilled water. 25 ml of this solution was then titrated with standard 0.1N sodium thiosulphate solution, added gradually with constant shaking until the yellow solution turned almost colourless. Two drops of freshly prepared starch indicator was added and titration continued in drops until the blue black colour entirely disappeared. Blank determinations were conducted [7].

The Iodine value was calculated using:

Iodine value (IV) = (B-S)×N×126.9 / Weight of sample (in g)

Where, B = Blank titre value (ml), S = Sample titer value (ml) and Normality of $Na_2S_2O_3$ = 0.1N.

2.6 Peroxide value (PV)

Oil sample (5.0 g) was accurately weighed into a conical flask, and dissolved in solvent mixture containing 12 ml chloroform and 18 ml glacial acetic acid. To the solution 0.5 ml of a saturated aqueous potassium iodide solution was added. The flask was stoppered and allowed to stand for 1 min. 30 ml of water was added and the solution was titrated with 0.1 M sodium thiosulphate solution until the yellow colour had almost gone. About 0.5 ml of starch solution was introduced and titration continued with the reagent added slowly until the blue black colour disappeared. During the titration, the flask was continuously and vigorously shaken to transfer the liberated Iodine from the chloroform layer to the aqueous layer. A blank titration was also performed, and the peroxide value was obtained from the formula [7]:

Peroxide value = F×(A-B)×10 / Weight of oil (in g)

Where F = Factor of 0.1N $Na_2S_2O_3$, A = Sample titer value and B = Blank titer value.

2.7 DPPH –free Radical scavenging activity

Different oil samples (20µl corresponding to 10mg) were added with 0.5ml of methanolic solution of DPPH and 0.48ml of methanol. The reaction mixture was allowed to stand at room temperature for 30 minutes. Methanol served as blank and DPPH in methanol without the leaf extracts served as positive control. After incubation, the discolouration of the purple colour was read at 518nm in a spectrophotometer. The per cent extent of radical scavenging was calculated using the formula,

DPPH Scavenging activity (%) =
A control – A sample / Acontrol X 100

Where Acontrol is the optical density of control (DPPH + Methanol).

3. Results and Discussion

Physicochemical Properties

3.1 Moisture Content

Moisture content is a widely used parameter in the processing and testing of food. The moisture content for unrefined and refined oils such as coconut oil, groundnut oil, gingely oil were found to be 4%, 2%, 2%, 2%, 12%, 2% respectively. It is an index of the water activity of many foods. A major aim of processed food item is to keep its moisture content very low so that it can be stored or preserved for long periods of time [8].

The edibility of crude and refined oils such as coconut oil, groundnut oil and gingely oil could not be ascertain without testing for other physicochemical parameters such as the peroxide value, Iodine value, saponification value, acid value and refractive index. The results of these physicochemical analyses of the oils were shown in table 1.

3.2 Saponification Value

Saponification value (SV) measures the average molecular weight of fatty acids present in the oil. The results show that Saponification value of refined oils are significantly lower when compared to that of unrefined oil. This difference generally could be due to the neutralization of fatty acids which may have resulted from hydrolysis of the oil sample [9].

3.3 Acid Value

The acid value for unrefined and refined edible oils such as in coconut oil, groundnut oil, gingely oil, the values were found to be 3.74meq/kg, 0.748meq/kg, 2.057meq/kg, 0.467meq/kg, 3.27meq/kg, 0.92meq/kg respectively. The results show that acid value of refined oils are significantly lower when compared to that of unrefined oil. Acid value of the edible oils should not exceed 4 mg KOH/g [10]. Acid values are used as an indicator for edibility or otherwise of oils and suitability for use in industries [1].

3.4 Iodine Value

Iodine value is a measure of the extent of unsaturation of fatty acid present in fat and oil. The results show that iodine value of refined oils are significantly higher when compared to that of unrefined oil. The degree of unsaturation increases progressively as a result of refining which reduced the level of impurities in crude oil thereby increased its iodine value [11]. The progressive reduction in Iodine value usually could be attributed to lipid oxidation. The higher the Iodine value, the higher the degree of unsaturation. When Iodine value is lower, it means that the double bond of the polyunsaturated fatty acid (PUFA) of the oil had been attacked and oxidation of the oil had taken place. Thus, there is progressive reduction of the nutritional value of the oil. Oils rich in unsaturated fatty acids have been reported to reduce heart diseases associated with cholesterol [12]. Although, Falade *et al*. (2008), [13] explained that high Iodine values also have its own disadvantages; for instance, the oil will be more susceptible to oxidative deterioration thereby making them difficult to store.

Table 1: Physicochemical properties of refined and unrefined edible oils

Experiment	Coconut oil (R)	Coconut oil(UR)	Groundnut oil (R)	Groundnut oil (UR)	Gingely oil (R)	Gingelyoil (UR)
Moisture content (%)	2	4	2	2	2	12
Saponification Value (mg KOH/kg)	142.4±2.04	164.49±3.18	111.07±2.86	149.5±2.47	164.09±2.91	175.31±3.15
Acid value (mg KOH/g)	1.748±0.14	3.74±0.36	1.467±0.11	2.057±0.14	1.92±0.16	3.27±0.22
iodine number (g I_2/100g oil)	55.83±1.82	20.81±0.63	84.769±1.94	79.43±1.73	147.2±2.18	106.59±1.85
Peroxide value (meq O_2/kg)	1.08±0.01	1.16±0.02	1.04±0.02	1.08±0.01	1.04±0.01	1.12±0.03

Table 1 shows the saponification value, acid value, iodine number and peroxide value of different refined and unrefined oils

3.5 Peroxide Value

Table 1 shows the peroxide value of unrefined and refined oils. The results show that peroxide value of refined oils are significantly lower when compared to that of unrefined oil. The peroxide value is used as an indicator of deterioration of oils. Fresh oils have peroxide values lower than 10 meqO_2/kg and before oil becomes rancid, its peroxide value must be between 20 and 40 meqO_2/kg [1]. Peroxide value is frequently used to measure the progress of oxidation in oil oils but not their stability. Therefore high peroxide value is an indication of high oxidative rancidity. Low peroxide value of the oil samples indicates its high resistance to peroxidation and low rate of spoilage [11].

Table 2: DPPH free radical scavenging activity of refined and unrefined edible oils

Radical scavenging activity concentration %	Coconut oil (R)	Coconut oil (UR)	Groundnut oil (R)	Groundnut oil (UR)	Gingely oil (R)	Gingely oil (UR)
1:1	82.7±1.02	62.5±1.64	96.5±1.85	78.5±1.07	92.8±1.27	72.7±1.15
1:2	46.9±0.95	32.5±1.22	47.5±0.84	40.1±0.39	39.3±1.18	35.4±0.74
1:4	22.2±1.33	18.5±0.84	26.3±0.97	23.2±0.87	20.6±1.04	19.3±0.83

Table 2 shows the DPPH free radical scavenging activity of different refined and unrefined oils Antioxidant plays an important role in inhibiting and scavenging free radicals, thus, providing protection to human against infection and degenerative diseases. DPPH is usually used as a substrate to evaluate the antioxidative activity. The antioxidant activity of different oils such as coconut oil, groundnut oil, gingely oil in three different concentrations in its unrefined and refined forms are shown in table 2.At a concentration of 0.5 mg/mL, the DPPH free radical scavenging activity of unrefined and refined oil was as follows: Groundnut oil > gingely oil > coconut oil. The results also indicate that the refined oils have significantly higher DPPH scavenging activity than unrefined oils. This indicates that the oils are the good sources of antioxidants and can prevent radical related pathological damage, especially breakdown of biomolecules and DNA by Lipid peroxidation that may lead to arteriosclerosis, carcinogenesis and inflammation [14].

Vegetable oils in their natural form possess constituents that function as natural antioxidants. Amongst them are ascorbic acids, -tocopherole, -carotene, chlorogenic acids and flavanols [15]. Antioxidants function either by inhibiting the formation of free alkyl radicals in the initiation step or by interrupting the propagation of the free radical chain [16]. Numerous experimental works have established the positive effect of anti-oxidants on the oxidative stability of vegetable oils for both edible uses and industrial uses. Measuring fatty acid formation and the measurement of peroxide values as a means of monitoring oxidation, results indicate an inhibitive effect on oxidation [15]. These tests and their findings suggest strongly the possibility of having in these plants a viable source of natural antioxidants of high performance [17].

4. Conclusion

The decrease in saponification value, acid value and peroxide value of refined oils when compared to that of unrefined oil indicate that the stability of the refined oils is higher than the unrefined oils. The higher value of iodine number of refined oils when compared to that of unrefined oil indicate the higher saturation of refined oil. The DPPH free radical scavenging activity show that the refined oils have higher antioxidant property than unrefined oil. Further the higher free radical scavenging activity of the groundnut oil when compared to other oils reveals the significantly higher antioxidant property of this oil.

5. References

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