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Influence of heat processing methods on the nutrient composition and lipid characterization of groundnut (*Arachis hypogaea*) seed pastes.

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Abstract

The effects of heat processing methods on the proximate composition, caloric value, mineral concentrations, vitamins A and C levels and lipid characterization of seed pastes of Arachis hypogaea were investigated. Moisture content was highest (25.2 ± 0.36%) in boiled seeds (BS) followed by raw seeds (RS) (4.58± 0.24%) and was lowest (1.21 ±0.20%) in fried seeds (FS) while ash ranged from 1.31 ± 0.01% in BS to 2.15 ± 0.07% in FS. Protein was highest in FS (28.45±0.21%) followed by RS (26.40 ± 0.18%) and lowest in BS (18.64±0.22%). RS had the highest crude fat of 51.1 ± 0.16% while BS had the lowest value of 25.23 ± 0.38%. Total carbohydrate was lowest in RS followed by FS and the highest value of 29.62 ± 0.30% in BS. The energy content in kcal/100g sample was in the order RS > FS > BS. The seeds were found to be good sources of copper, iron, zinc, sulphate and chloride. Boiling and frying had no significant effect (P>0.05) on copper but significantly (P< 0.05) decreased iron and zinc. Boiling significantly (P<0.05) decreased sulphate and chloride which were significantly increased by frying. Boiling decreased the concentrations of vitamins A and C which were further decreased by frying. The % free fatty acid, peroxide value, acid value and iodine value were highest in RS and the lowest values were obtained in FS, BS, FS and FS respectively. No significant difference (P > 0.05) was obtained in the saponification number of the three samples analyzed and values ranged from 161.3 ±2.92 in RS to 163.0 ± 2.60 in FS. Heat processing (boiling and frying) generally decreased significantly (p<0.05) the crude protein, crude fat, caloric value, Fe, Zn, vitamins A and C as well as % free fatty acid and peroxide value but had no significant effect on Cu, acid value, iodine value and saponification number. However, frying increased significantly (P<0.05) the dry matter, ash, SO_4^{2-}, Cl^- and unsaponifiable matter. These findings may offer scientific basis for the use of the processed seeds as food for humans and oil extracts for the manufacture of industrial products.

Key words: Heat processing methods, *Arachis hypogaea* seeds, nutrient composition, lipid characterization.

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INTRODUCTION

Groundnut (*Arachis hypogaea*) is a leguminous plant grown in Nigeria mainly for its seeds though farmers use its leaves and shells as organic mulch. The seeds are eaten raw, boiled, fried and roasted. In most Nigerian homes, women use the seed paste in soups and stews as a thickener. Like soyabean (Glycine max), groundnut (Arachis hypogaea) is an industrial crop used mainly as a source of oil (1). The cake or residue obtained after the oil is extracted has been reported to be high in protein and used as supplement in animal feed (2). Groundnut cake obtained after frying the cake in oil and which the Hausa people of Nigeria call Kulikuli is used as a delicious snack for humans and can be used as supplement in other dishes, and as a food, groundnut is very high in energy due to its high fat and protein content (1)

Methods that can be used to characterize fats and oils (lipids) include the determination of certain important parameters namely free fatty acid content, total acidity (acid value), iodine number, saponification number and unsaponifiable matter. The free fatty acid (FFA) of an oil or fat is half its acid value. It is the fatty acid present in oil following hydrolysis by lipase and which has not been neutralized. The FFA is a measure of the amount of free fatty acid in a fat or oil. The acid value of an oil or fat is the number of milligrams of potassium hydroxide (KOH) required to neutralize the free acid in 1.0g of the oil and is a a measure of the total acidity of the oil arising from all the constituent fatty acids that make up the fat or oil. The acid value measures the extent of decomposition of the glycerides in the oil by lipase. Rancidity is accompanied by the formation of FFA and so acid value or FFA determination is employed as a means of knowing the quality and edibility of oil.

The iodine number of an oil is the number in grams of iodine which can be absorbed by 100g of the oil, and it measures the amount of unsaturated fatty acids occurring in the oil. Iodine does not react readily with the double bonds of oil/fat molecule and the quantity of iodine absorbed by oil is an index of its degree of unsaturation. Low iodine number implies the presence of few unsaturated bonds and hence low susceptibility to oxidative rancidity. Therefore, the higher the iodine value the higher the degree of unsaturation and hence the greater the tendency of the oil/fat to undergo oxidative rancidity. The latter is a chemically induced autolysis (self deteriorative process) in which non-conjugated polyunsaturated oils react with oxygen to give peroxides which abstract proton from the system to produce hydroperoxides that build up and consequently breakdown to produce odourous aldehydes, ketones, alcohols and acids which cause the off-flavour in oxidized fats and oils (3)

$$\text{Polyunsaturated oil} + O_2 \longrightarrow \text{Peroxide} - H^+$$

$$\downarrow$$

$$\text{Hydroperoxides}$$

$$\downarrow$$

$$-CHO + {>}C=O + -COOH + R-OH$$

aldehyde ketone acid alcohol

The process is accelerated by high temperature, ultraviolet light and some divalent metals (3). Hydrolytic rancidity occurring mainly in oil extracted with water is an enzyme catalysed reaction in which fats in the presence of water are hydrolysed to give glycerol (a trihydric alcohol) and free fatty acids (3).

The saponification number is the number of mg KOH required to hydrolyse or saponify 1.0g of fat/oil. The unsaponifiable matter are oil-solube materials which after saponification are not soluble in water but soluble in the solvent (usually petroleum ether or diethyl ether) used for the determination. The poly unsaturated to saturated fatty acid ratio of groundnut oil is 2:1 and the oil has also been shown to be useful in cooking and in the industrial manufacture of margarine, salad oils, mayonnaise and cosmetics (4).

Free fatty acids, total acidity, iodine number, peroxide value, saponification number, and unsaponifiable matter are usually determined with a view to ascertaining the quality and establishing the nature of individual fats and oils before they are deemed suitable for either domestic or industrial consumption (5). There is little or no information in literature on the nutritional value and quality of *Arachis hypogaea* seeds processed for consumption by methods of boiling and frying. The present work was therefore designed to investigate the effect of boiling and frying on the proximate composition, energy content, mineral concentrations and vitamins A and C levels of the seed pastes of *Arachis hypogaea.* The paper also reports the influence of these processing methods on the lipid characterization of the seed pastes investigated.

MATERIALS AND METHODS

Sample: The *Arachis hypgaea* seeds were purchased from Owerri main market in Imo State in the southeast geopolitical zone of Nigeria where it is cultivated for food. The seeds were wrapped in black polyethene bag, sealed in a clean dry air-tight container and stored in a refrigerator (4°C) for three days before processing and analyses.

Sample processing: The wholesome seeds were sorted and divided into three lots of 400g each. One lot which served as the raw sample was ground into a paste using a food grinder (Model MX 491 N, National). The second lot was boiled in tap water for 25 minutes and ground into a paste, while the third lot was fried in hot sand for 25 minutes and also ground into a paste. The pastes were analyzed immediately they were produced.

Analyses of sample: The methods of the Association of Official Analytical Chemists (6) were used to determine moisture level, ash, crude protein and crude fat. Moisture content was obtained by heating three 4.0g portions of the sample in an oven (Plus 11 Sanyo, Gallenkamp PLC England) at 105°C until a constant weight was obtained. Ash was determined by the incineration of three 2.0g samples in a muffle furnace (Model LMF4 from Carbolite, Bamford, Sheffield, England) at 600°C for 4.0 hours when a light – grey ash was obtained. Crude protein (% Nitrogen x 6.25) was obtained by the method of AOAC (6) using three 2.0g portions of the sample, while crude fat was determined by exhaustively extracting three replicates of 5.0g samples in the soxhlet apparatus using petroleum ether (B.P. range 40 - 60°C). Total carbohydrate was calculated by difference. Energy content was obtained by multiplying the mean values of crude protein, crude fat and total carbohydrate by the Atwater factors of 4, 9, 4 respectively, taking the sum of the products and expressing the result in kilocalories per 100g sample as reported by Edem *et al* (7) and Onyeike *et al* (8). The amount (x) in gram of each of raw and processed samples that would provide an energy value of 2750 kcal was obtained by multiplying 2750 by 100 and dividing the product with the total energy content of the sample expressed in kcal/100g sample. For example, in raw groundnut seeds having energy content of 631.6 kcal per 100g (Table 1),

$$x = \frac{2750 \times 100g}{631.6} = 435.4g$$

Again, if 100g of this raw sample provide energy of 631.6 kcal, then the consumption of the sample at 195g daily would provide an energy value of

$$\frac{631.6 \times 195}{100} = 1231.6 \text{ k cal}$$

The minerals Cu, Fe and Zn were determined by atomic absorption spectrophotometry as described by Agte *et al* (9) using an atomic absorption spectrophotometer (Perkin-Elmer Model 2380, USA). Sulphate was determined by the turbidimetric method of Butters and Chenery (10) in which B_aSO_4 was precipitated and the degree of turbidity measured at 470nm as an index of sulphate concentration. Chloride (Cl^-) in the sample was determined by the Argentimetric method based on Mohr's procedure as outlined by Bowley (11). Here, 25.0ml of the sample extract and a blank for comparison, were each titrated with a standard solution of silver nitrate (0.10 M $AgNO_3$) reagent to a brick-red end point using potassium chromate solution as an indicator. Vitamin A was obtained by the AOAC (6) method. The percentage decrease in each of vitamins A and C content due to heat processing was obtained by subtracting the value of the processed sample from that of the raw, dividing the difference with the value for the raw and multiplying the quotient by 100. The 2,6-dichlorophenol indophenol visual titration method of Davis and Kramer (12) as reported by Onyeike and Onwuka (13) was used to determine vitamin C in the sample extract.

The percentage free fatty acid, peroxide and acid values were determined by the method of Davine and Williams (14). The iodine value was determined by the method of Strong and Kock (15), the saponification number by the procedure of Williams (16) while the unsaponifiable matter was obtained by the method of FAO (17)

Data Analyses: Data were statistically analyzed by a one-way analysis of variance (ANOVA) using SPSS/PC + package. Differences between means were compared by use of Duncan's (18) Multiple range test. Significance was accepted at a p-value of less than 0.05 ($p < 0.05$).

RESULTS AND DISCUSSION

The results of proximate composition and caloric values of raw and heat processed seed pastes of Arachis hypogaea (Ah) are shown in Table 1. Boiling significantly increased moisture content ($p<0.05$) while frying significantly decreased it ($p<0.05$). Fried samples would therefore store for a longer time without spoilage compared to boiled ones. Ash was highest in the fried seeds and lowest in the boiled seeds but values for raw and boiled seeds did not differ significantly ($P > 0.05$). Protein was highest in fried seeds (FS) (28.45 ± 0.21%) and lowest in boiled seeds (BS) (18.64±0.22%) while crude fat was highest (51.1± 0.16%) in raw seeds (RS) and lowest (25.23 ± 0.38%) in BS. It is thought that boiling may have resulted in the lowest amounts of ash, crude protein and crude fat due to water absorption resulting in dilution. Boiling for 25min resulted in such great losses because the seeds may have lost their structural integrity to lead to 5.76%, 29.4% and 50.6% loss in ash, crude protein and crude fat respectively. Total carbohydrate was increased significantly by boiling and frying. Caloric value was highest in RS followed by FS and was lowest in BS. The lowest value of 420.1 kcal/100g sample in BS is attributable to the lowest levels of crude protein and crude fat in the sample (Table 1). Consumption of BS of Ah is recommendable to individuals suffering from overweight and hyperlipidemia while the consumption of FS is recommendable to patients suffering from protein – energy malnutrition. Although the RS have the highest amount of energy of 631.6 kcal/100g sample the consumption of raw groundnut seed should not be entirely preferable to fried and boiled seeds due to the presence of antinutrients or toxicants (hydrocyanic acid, oxalates, phytates) which have been found in natural association with groundnut seeds (19, 20). In Nigeria today, most people especially the low income earners or people of the low socioeconomic status eat Ah seeds raw, boiled or fried either alone or with garri, biscuits, bread and banana as snacks to delay hunger. The energy values (kcal/100g sample) of 631.6, 420.1 and 586.6 for RS, BS and FS indicate that 435.4g, 654.6g and 468.8g of these raw and processed samples would, respectively, provide 2750 kilocalories – an energy value which falls within the range of the daily calorie requirement of 2500 to 3000 kilocalories for adults (21). It is interesting to note that the consumption of these samples at only 195g per day would provide energy values of 1231.6, 819.2 and 1143.9 kcal for RS, BS and FS respectively. These values would meet the Food and Agriculture Organization's (22) recommended energy range of 800 to 1200 kcal for adults.

Results in Table 2 show that the samples are good sources of Cu, Fe, Zn, SO_4^{2-} and Cl^-.

Boiling and frying did not significantly ($p>0.05$) decrease the concentration of copper but significantly ($p< 0.05$) decreased those of iron and zinc. The concentrations of sulphate and chloride anions were significantly ($p< 0.05$) decreased by boiling while frying significantly ($p<0.05$) increased their concentrations. The effects of the heat treatments on vitamins A and C concentrations of Ah seeds are shown in Table 3

Table 1: Proximate composition (%)* and caloric values of raw and heat processed seed pastes of *Arachis hypogaea*

Constituent	Raw seeds(RS)	Boiled seeds (BS)	Fried Seeds (FS)
Moisture	4.58 ± 0.24^{b}	25.20 ± 0.36^{a}	1.21 ± 0.20^{c}
Dry matter	95.42 ± 0.25^{b}	74.80 ± 0.35^{c}	98.79 ± 0.21^{a}
Ash	1.39 ± 0.01^{b}	1.31 ± 0.01^{b}	2.15 ± 0.07^{a}
Crude Protein	26.40 ± 0.18^{a}	18.64 ± 0.22^{b}	28.45 ± 0.21^{a}
Crude fat	51.10 ± 0.16^{a}	25.23 ± 0.38^{c}	40.00 ± 0.40^{b}
Total carbohydrate	16.53 ± 0.24^{b}	29.62 ± 0.30^{a}	28.19 ± 0.20^{a}
Caloric value (kcal/100 g sample)	631.6^{a}	420.1^{c}	586.6^{b}

** Values are Means ± standard deviations of triplicate determinations. Values in the same row having the same superscript letters are not significantly different (p < 0.05).*

Table 2: Mineral concentrations (ppm)* of raw and heat processed seed pastes of *Arachis hypogea*

Constituent	Raw	Boiled	Fried
Copper	1.27 ± 0.01^{a}	1.25 ± 0.00^{a}	1.22 ± 0.01^{a}
Iron	0.22 ± 0.01^{a}	0.11 ± 0.04^{b}	0.17 ± 0.03^{b}
Zinc	0.10 ± 0.00^{a}	0.05 ± 0.03^{b}	0.03 ± 0.00^{b}
Sulphate	7.90 ± 0.02^{b}	5.96 ± 0.04^{c}	10.84 ± 0.08^{a}
Chloride	0.36 ± 0.01^{b}	0.18 ± 0.00^{c}	0.87 ± 0.01^{a}

** Values are Means ± standard deviations of triplicate determinations. Values in the same row sharing the same superscript letters are not significantly different (p < 0.05.)*

Table 3: Vitamins A and C levels* of raw and heat processed seed pastes of *Arachis hypogaea*

Constituent	Raw	Boiled	Fried
Vitamin A (mg/100g)	0.104± 0.00[a]	0.033 ± 0.00[b] (68.3)	0.024 ± 0.01[b] (76.9)
Vitamin C (mg/100g)	4.52 ± 0.04[a]	4.01 ±0.03[b] (11.3)	3.55 ± 0.04[c] (21.5)

** Values are means ± standard deviations of triplicate determinations. Values in the same row having the same superscript letters are not significantly different (p <0.05). Values in parenthesis indicate percentage decrease in the vitamins due to the heat processing methods employed.*

Table 4: Lipid characterization* of raw and heat processed seed pastes of *Arachis hypogaea*.

Constituent	Raw (RS)	Boiled (BS)	Fried (FS)
% Free fatty acid as oleic acid	2.68 ± 0.20[a]	2.12 ± 0.21[b] (20.9)	2.00 ± 0.00[b] (25.4)
Peroxide value (mg/g oil)	27.0 ± 4.20[a]	18.0 ± 2.80[b] (33.3)	19.0 ± 1.40[b] (29.6)
Acid value (mg KOH/g oil)	3.20 ± 0. 0.57[a]	2.85 ± 0.00[a] (10.9)	2.80 ± 0.00[a] (12.5)
Iodine number (mg/100g)	87.6 ± 8.0[a]	84.9 ± 4.3[a] (3.08)	84.7 ± 4.0[a] (3.31)
Saponification number (mg KOH/g oil)	161.3 ± 2.92[a]	162.3 ± 2.75[a] (0.62)	163.0 ± 2.60[a] (1.05)
Unsaponifiable matter (%)	1.60 ± 0.35[b]	1.86 ± 0.21[b] (16.3)	2.48 ± 0.20[a] (55.0)

** Values are Means ± standard deviations of triplicate determinations. Values in the same row having the same superscript letters are not significantly different (p < 0.05). For percentage free fatty acid, peroxide value , acid value and iodine number, values in parenthesis indicate percentage decrease while for saponification number and unsaponifiable matter, values in parenthesis represent percentage increase in the raw groundnut seed pastes due to the heat processing method employed.*

Boiling and frying decreased vitamin A, respectively by 68.3% and 76.9%. For vitamin C the decrease was 11.3% when boiled and 21.5% when fried. Common deficiency signs of vitamin A include failure of young animals to grow and of the bones and nervous systems to develop properly leading to unsteady gait (ataxia), eye irritation and dry skin, degeneration of the kidneys and various glands, sterility in females and reproductive failure in males where sperm cell formation is affected (23). Xerophthalmia ("dry eyes") is an early symptom of deficiency which lead to blindness in infants and young children while in adults early deficiency sign is night blindness or inability to see in dim light; young animals are most susceptible to vitamin A deficiency which in adults is not readily produced since the liver is capable of storing sufficient vitamin A to last for months or even years (23). Scurvy is a disease due to lack of ascorbic acid, and it is characterized by hemorrhages of skins, gums and joints, inability of collagen to form and failure of wounds to heal easily (24). It has also been reported that the deficiency of vitamin C results in a long-known avitaminosis (scurvy) characterized by rupture of blood capillaries, bleeding (haemorrhage) of the skin and mucosas, inflammation of the gum, loosening of the teeth, painful swellings of the joints and decreased resistance to infectious diseases (25). Most hungry people consume the Ah seeds in the raw (unprocessed) state. If Ah seed meal is to be designed for patients suffering from lack of vitamins A and C, it is recommended that it be taken in the raw state provided the levels of natural toxicants are quite low to cause any physiological problem, and further tests including sensory evaluation on humans and microbiological tests carried out. For instance, the raw groundnut seeds is not as acrid and does not produce as much irritation to the digestive track compared to raw cocoyam tuber (26), and may hence contain relatively lower concentration of oxalate. Again, the raw seeds are not bitter to taste and may hence not contain physiologically untolerable concentrations of tannins and alkaloids. Vitamin C had previously been shown to be destroyed at high temperatures under conditions that permit access to oxygen from the atmosphere (27). Factors, which readily oxidize and destroy the biological activity of Vitamin C include oxygen, neutral or alkaline pH, metallic ions and light – the rate of destruction of which is accelerated by increase in temperature (12). Recent study has also shown that cooking significantly ($P< 0.05$) decreased the concentration of ascorbic acid in African oil bean seeds, melon seeds, castor oil seeds and fluted pumpkin seeds, and values were further decreased as the cooked samples were subjected to fermentation (13).

The results of lipid characterization of raw and heat processed seed pastes of *Arachis hypogaea* are presented in Table 4. The percentage free fatty acid (% FFA) as oleic acid was highest (2.68± 0.20%) in RS. Boiling significantly ($p < 0.05$) decreased percentage free fatty acid which was further decreased by frying. Values for boiled and fried seeds were however not significantly ($p > 0.05$) different. Each of the oils from raw, boiled and fried seed pastes of Ah had % FFA below the maximum limit of 5.0% reported for high grade Nigerian palm oil (28) indicating that the oils are good edible oils. The % free fatty acid ranged from 2.00 ± 0.00% in oils from fried seeds to 2.68± 0.20% in oils from raw seeds showing that the oils investigated are good cooking oils. It has been reported that the nutritional value of a fat depends, in some respects upon the amount of free fatty acids which it develops (e.g. the amount of butyric acid in butter); and in the tropics where vegetable oils are the most common dietary lipid, it is desirable to ensure that the free fatty acid content should lie within limits of 0.0 to 3.0% (29). Boiling and frying significantly ($p < 0.05$) decreased the peroxide value, but values for boiled and fried seeds were not significantly different. Pearson (30) reported that oils become rancid when peroxide values range from 20.0 to 40.0 mg/g oil while Ojeh (31) showed oils with high peroxide values to be unstable. It can therefore be deduced that boiling and frying of Ah seeds would enhance the nutritional quality and keeping quality of oils from the seed pastes of groundnut seeds. Boiling decreased the acid value which was further slightly decreased by frying but the decrease was not in each case significant ($p <0.05$). The acid value is a measure of total acidity of the system which may involve contributions from all the constituent fatty acids that make up the glyceride molecule (5). The oils investigated especially those from fried and boiled samples would be very useful in industries that manufacture soap (14), in cooking and in industries that manufacture blue band margarine, mayonnaise, cosmetics and salad oils (4) due to their relatively low acid values compared to those obtained from the seeds of *Xylopia aromatica* (16.0 ± 0.3), P*iper guinenses* (21.0 ± 1.0) and *Chryosophyllum albidum* (12.1± 0.4) by Dosumu and Ochu (32).

Heat processing did not significantly (P> 0.05) affect the iodine value and the saponification number. The high iodine values which ranged from 84.7 ± 4.0 in fried to 87.6 ± 8.0 mg/100 g in raw samples indicate the presence of highly unsaturated bonds. Based on the report of Eka (33), it may be sensible to infer that the oils from raw, boiled and fried Ah seed pastes investigated are high quality edible oils. The iodine value for groundnuts investigated was highest in oils from raw seeds (87.6 mg/100 g) followed by boiled seeds (84.9 mg/100 g) and was lowest in oils from fried seeds (84.7 mg/100 g). These values which did not differ significantly (p>0.05) are high, making groundnut oil a high quality edible oil because of the high degree of unsaturation due probably to the high contents of palmitoleic and oleic acids. The saponfication number was highest in fried (163.0±2.60) and lowest in raw (161.3± 2.92) oil extracts. These values would indicate that the samples contain a large number of fatty acids of low molecular weight and hence useful in soap industries and in the manufacture of lather shave creams (33). The higher value of saponification number in FS as compared with RS and BS may be due to a relatively higher degree of enzyme denaturation in oil extracted from FS. In the oil from RS paste, the fat-hydrolyzing enzyme (lipase) in its active non-denatured state may have in part mediated the hydrolysis of the oil thereby decreasing the amount in mg KOH required to saponify 1.0g of the oil. The high temperature of boiling and frying as forms of heat processing may have denatured the fat-hydrolysing enzyme with a higher degree of denaturation or enzyme inactivation occurring in the fried oil. This would therefore increase the amount of milligram of potassium hydroxide required to hydrolyze 1.0g of the oil.

The relatively lower saponification value in BS compared to FS may be due to partial enzyme hydrolysis of oil in BS due to the presence of residual water which may have aided hydrolysis resulting in lower amount of mg KOH required to saponify 1.0g of the oil. Hence, the lower saponification number in BS. In oil from FS, all the elements of water may have been removed by the higher temperature of frying as compared with boiling. This could have resulted in a drier sample of oil from FS compared to BS and hence more number of mg KOH required to hydrolyze or saponify 1.0g of oil from FS.

The unsaponifiable matter present in the oils which after saponification by caustic alkali (KOH) and extraction with a suitable solvent remained non-volatile on drying at about 90°C may include high molecular weight alcohols, hydrocarbons and sterols such as phytosterols and cholesterol as well as foreign organic matter which do not volatilize at 100°C. Values of unsaponifiable matter obtained in this investigation ranged from 1.60 ± 0.35% in RS to 2.48 ± 0.20% in FS. These raw and processed groundnut seed oils which contain less than 3.0 % unsaponifiable matter could therefore be adjudged oils of normal purity and good edibility.

Conclusion

It can be concluded that Ah seeds are good sources of nutrients especially crude fat, crude protein and ash, calorie, minerals, vitamins A and C as well as oil extracts for domestic and industrial uses. Heat processing improved the keeping quality, and utilization of the seeds and their oil extracts for domestic and industrial purposes.

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