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Afolabi, et al. (2018).Comparative study of the antioxidant potentials of grape seed and peel extracts. 13(1): 39-44.

Comparative study of the antioxidant potentials of grape seed and peel extracts.

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Abstract.

A comparative study of the antioxidant potentials of extracts from grape seed and peel on lipid oxidation is reported in this study. Grape fruit sample was collected and the seed and peel of the fruit were separated and oven dried. This was further subjected to grinding and finally sieved to obtain a particle size of 500 µm. The extraction of antioxidant was carried out in a soxhlet extractor using methanol as the extraction solvent. The elemental analysis of the grape seed and peel extracts revealed that potassium was the most dominant element with a composition of 86 and 90.1% respectively. The effect of the grape seed and peel extracts on the mixture of oil sample was evaluated by measuring the oxidation stability using Rancimat machine. The oxidation stability of the oil mixture sample without and with the addition of grape seed and peel extracts were found to be 67, 553 and 569 minutes respectively. Furthermore, the results of the peroxide value, pH and free fatty acid of the oil mixture without and with grape seed and peel extracts were carried out and antioxidant effectiveness of the grape seed and peel extract calculated after 50 days to be 29% and 30% respectively. This result clearly showed that antioxidant potential of grape peel extract is slightly higher than that of grape seed extract.

Key words: Antioxidant, Extraction, Fat and Oil, Grape fruit, Oxidation, Solvent
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Introduction.

Antioxidants are molecules with ability to inhibit or slow the oxidation process of other molecules. Free radicals produced by oxidation reaction are caused by the transfer of electrons from a substance to another that is reduced and thereby initiates a chain reaction that causes damage to cells. Antioxidants has been found to bind metals, scavenging species that initiates oxidation, stops high-energy oxygen species by preventing peroxides formation, or decomposition of lipid peroxides (Hamid *et al.*, 2010). Antioxidants are widely used as ingredients in dietary supplements to maintain human health and prevent diseases such as cancer and coronary heart diseases. Beside medicinal importance, natural antioxidants extend its applications in the industries such as food preservatives, cosmetics production and in preventing the degradation of rubber and gasoline. (Bjelakovic *et al.*, 2007).

For example, lubrication oil is expected to remain stable and shouldn't dry up like paints. Therefore, small quantities of antioxidants such as phenol or amine derivatives are usually added as an additive. Lipid oxidation is a major cause of food spoilage as it reduces the shelf life of foods. Lipid oxidation occurs during refining and oil extraction and resulting in the formation of lipid hydro peroxides. Some of the advantages in preventing lipid oxidation includes reduction of raw material wastage and nutritional loss, and increases the range of lipid usage for specific product as well as extends the product's shelf life. Antioxidants help to preserve food palatability, nutrition and satiety (Padmaja, 2013).

The grape fruit (*Citrus paradisi*) is a subtropical citrus tree usually grown for its fruits to be consumed by man and animals (Saalu *et al.* 2010). Therefore, the grape fruit is found to be increasingly popular and provides significant source of natural antioxidants. The extract of grape fruit contains high level of vitamin E, C and bioflavonoids. These compounds have been found to be effective antioxidants collectively and individually. Bioflavonoids form a class of benzo-gamma-pyrone derivatives that have high pharmacological potency (Lee *et al.*, 2002). The antioxidant activities of bioflavonoid complements extend and sometimes synergize the antioxidant activities of vitamin C, E and carotenoids and this make them a useful nutritional component (Ajila *et al.* 2007; Borang, 2010).

This research work is aimed at the extraction, characterization and antioxidant investigations of oven dried grape seeds and peels using soxhlet apparatus. The extracts from grape seed and peel were then characterized using Atomic Absorption Spectrophotometer for elemental analysis. The comparative studies of the effect of the grape peel extract with that of

the grape seed on lipid were then carried out using Rancimat method for oxidation stability index and peroxide value test, acid value test and pH performed.

Materials and Methods.

The grape fruit sample was sourced from Vunchi in Lavun Local Government of Niger State, Nigeria. Groundnut oil and animal fat used were bought from local markets in Bida and Minna, Niger state respectively. Grape fruit sample was then taken to the School of Agriculture and Agricultural Technology, Federal University of Technology Minna, Niger state for clarification and identification. The grape fruit was washed and peeled, thereafter separated into grape seed and peel. The grape peel sample was weighed and oven dried for 48 hours at 60 °C, thereafter its moisture content determined. The dried grape peel was milled by a combination of small mortar and pestle, and grinder into a mesh size of 0.5 mm. The ground grape peel was enclosed in a filter paper for extraction. The same procedure was carried out on the grape seed sample with the exception that it was oven dried for 13 hours. The difference in drying time for the two samples is to ensure that the removal of moisture content to minimum value.

Extraction of Sample.

One variable at a time method was used for the solvent extraction of ground grape seed in a soxhlet extraction using methanol as the extracting solvent. The grape seed sample was weighted, sealed with a filter paper and thereafter extracted at optimum conditions established by Afolabi *et al;* (2016). The same procedure was carried out for soxhlet extraction of the grape peel sample. The preliminary work carried out by Afolabi *et al;* (2016) showed that the optimum extraction time, temperature and solid-solvent ratio for the extraction of grape peel is 180 minutes, 45°C and 10 g: 150 ml. However, the optimum conditions for the extraction of grape seed are 140 minutes, 60°C and 10 g: 200 ml. The extract mixture obtained after soxhlet extraction was filtered and evaporated to dryness in order to remove methanol under reduced pressure at 60 °C by a rotary evaporator. Thereafter, extracts obtained were placed in dark bottles and stored in refrigerator at 4 °C for further use (Hegazy and Ibrahium, 2012).

Determination of Elements present in the Grape Peel Extract.

Atomic Absorption Spectrophotometer (Accusys 211 model, USA) analysis was used in analyzing the elemental composition of the grape peel and seed extracts. The AAS analyses help in determining the composition of the grape seed and peel extracts and comparison made with extract obtained from other antioxidant rich fruits (Sykorova *et al,* 2009).

Preparation of Oil Mixture Sample.

In order to ascertain the antioxidant potential of extracts from the grape peel and seed, oil sample was prepared by mixing unsaturated groundnut seed oil with saturated cow fat in the ratio of 4:1 according to the method described by Akpan *et al;* (2015) and Wan (2009). This mixture is thereafter referred to as oil sample.

Evaluation of the Oxidation Stability of extracts from the Grape Peel and Seed.

The oil sample with extract was made by mixing the oil mixture and extract from grape seed in the ratio of 8:1 and referred to sample B. The same procedure was carried out for sample C for a mixture of grape peel with oil mixture. An evaluation of the oxidative stability of the oil mixture mixed with and without grape extracts was carried out using the Rancimat test. The oxidative stability was determined in 743 Rancimat apparatus from Metrohm according to ISO 6886:1997, utilizing a sample of 2.5 g. All samples were heated to 110 °C with an air flow of 10 L/h. (Farhooshi and Moosavi, 2007).

Evaluation of Lipid Oxidation of Grape Peel Extracts.

Lipid oxidation test was carried out on the oil sample mixed with and without grape extracts in order to evaluate the antioxidant potential of the grape peel and seed extracts. 5 ml of grape seed extract was added to 40 ml of oil sample prepared as in section 2.5 (sample B) and, 5 ml of grape peel extract added to 40 ml of oil sample for sample C. The pH, peroxide value and acid value tests were used to analyze

antioxidant effectiveness of the extracts from grape peel and seed on a mixture of groundnut seed oil and cow fat. The peroxide value and acid value tests were carried out according to the standard procedures stated by Etti *et al*, (2012), John (2010) and Fereidoon and Ying (2003).

The percentage of antioxidant effectiveness was calculated using the method described by Adegoke and Gopalakrishna (1998) from equation (1)

$$AE\ (\%) = \frac{(PVC - PVT)}{PVC} \quad (1)$$

where AE is the antioxidant effectiveness, PVC is the peroxide value of control sample and PVT is the peroxide value of test sample.

Results.

In this section, we summarize the results of the AAS analysis and oxidation stability test of the extracts (Table 1). In addition, antioxidant potentials of the grape seed and peel extracts on oil mixture samples are presented for a period of 50 days.

Table 1: AAS Analysis of grape seed and peel extracts

Elements Present	Na	K	Ca	P	Cu	Fe	Mn	Pb
Grape Seed Extract (PPM)	11.9	114.0	0.00	5.77	0.67	0.11	0.00	0.1
Grape Peel Extract(PPM)	8.6	196.0	2.6	6.28	0.3	0.1	0.01	0.1

Table 2: Oxidation stability of oil mixture with and without extracts

Oil Sample	67 minutes
Oil Sample with Grape Seed Extract	553 minutes
Oil Sample with Grape Peel Extract	569minutes

Table 3: Effect of peroxide value test on samples for a period of 50 days.

Sample	Day 3	Day 15	Day 35	Day 50
Oil Sample without grape extract (meq.g/kg of oil	3.10	3.60	4.00	4.50
Oil Sample with grape seed extracts(meq.g/kg of oil)	2.58	2.88	3.01	3.20
Oil sample with grape peel extract (meq.g/kg oil)	2.40	2.70	2.91	29.00
Antioxidant effectiveness for grape seed extract (%)	16.77	20.00	25.00	29.00
Antioxidant effectiveness for grape peel extract (%)	22.58	25.00	27.30	30.00

Table 4: Effect of free fatty acid test on samples for a period of 50 days.

Sample	Day 3	Day 15	Day 15	Day 50
Oil sample without extract (mgKOH/g of oil)	2.62	3.10	3.70	4.50
Oil sample with grape seed extract (mgKOH/g of oil)	2.42	2.77	3.30	3.55
Oil sample with grape peel extract (mgKOH/g of oil)	2.40	2.70	3.20	3.50

Table 5: Effect of pH test on samples for a period of 50 days.

Sample	Day 3	Day 15	Day 35	Day 50
Oil sample without grape extract	6.96	6.56	6.20	5.60
Oil sample with grape seed extract	6.88	6.50	5.62	4.45
Oil sample with grape peel extract	6.83	6.45	5.60	4.40

Discussions.

Atomic Absorption Spectrophotometer Analysis of Grape Seed and Peel Extracts.

The Atomic Absorption Spectrophotometer analysis of the major and minor elements present in the samples of grape peel and seed are presented in Table 1. The major element present in the grape peel and seed extracts is Potassium (K) with a percentage composition of 90.1 % in the grape peel extract as against 86% found in grape seed extract. The result in Table 1 also show that calcium and manganese are absent in the grape seed extract but present as minor elements in grape peel extract. This result is in agreement with the works of Gaitry *et al;* (2013), Borang, (2010) and Sykorova *et al.*, (2009), who all classified potassium as one of the major elements in antioxidant sample. However, elements such as Sodium (Na) and Phosphorus (P) are classified as intermediate and Copper (Cu), iron (Fe) and Lead (Pb) were found to be the minor elements based on their percentage composition in the AAS analysis.

Evaluation of Oxidation Stability of Oil Mixture.

The induction period of the oil mixture without extract and with grape peel and seed extracts was presented in Table 2. The induction period of oil mixture sample without any grape extract was found to be 67 minutes. This implies that the shelf life of oil mixture (a period whereby the oil sample is capable to resist oxidation) is 67 minutes. However, with the addition of the grape seed and peel extracts to the oil mixture, the stability of the oil mixture wan enhanced from 67 minutes to 553 minutes and 569 minutes respectively. This result is in agreement with the work of Delfanian *et al.*, (2015), who reported that the induction period of oil sample containing extract of fruits are higher than that of the control oil sample. The antioxidant activity index of the oil is the ratio of time required to oxidize a given sample heated at 110 °C with and without the presence of antioxidant.

This implies, the time when either a level of detectable rancidity or sudden change in the rate of oxidation occurring in the oil sample is hereby increase by 8.25 and 8.49 respectively. An important finding of this present study is that, antioxidant potential of the extract from grape peel is found to be higher than that of grape seed by 16 minutes and this translate into 0.24. This implies, extract from grape peel was able to stabilize oil mixture for a period of 16 minutes longer in comparison to that of the extract from grape seed.

Effect of Grape Extracts on Oil Mixture for a Period of 50 Days.

Analysis of the Peroxide Value Test.

The peroxide value is a measure of how lipid oxidation occurs; this is because peroxides are one of the major by products formed during lipid oxidation. The result of the effect of grape seed and peel extracts on the mixture of groundnut seed oil and cow fat are shown in Table 3. It was observed that there is a general reduction in the peroxide value of the oil sample without the extract in comparison with samples containing extracts. This implies addition of the grape seed and peel extracts slow down the formation of peroxide, thereby serve as an antioxidant. The result obtained in this work is in agreement with the study of Etti *et al.* (2012).

However, the grape peel extract is found to be more efficient in slowing down the formation of peroxide as the peroxide values obtained after 50 days duration was lower when compared with that of oil mixture mixed with grape seed extract. The peroxide value of samples without extract decreases from 3.1 to 2.4 and 2.58 meq.g/kg of oil at day 3 for samples with grape peel and seed extracts respectively. The same pattern is observed when comparing the peroxide values of samples without and with extracts for a period of 15, 35 and 50 days. The antioxidant effectiveness of grape peel extract is observed to be higher than that of grape seed extract as shown in Table 3. The antioxidant effectiveness of grape peel extract at day 3 is 22.58 % and increases to 25, 27.3 and 30 % at days 15, 35 and 50 respectively. However, antioxidant effectiveness of grape seed extracts increases from 16.77 to 20%, 25 and 29% at day 3, 15, 35 and 50 respectively.

Analysis of Free Fatty Acid Test.

The free fatty acid value of oil sample without extract decrease on comparison to that of oil samples with either grape seed or peel extracts. As shown in Table 4, at day 3 the free fatty acid value of oil sample is 2.62 mg KOH/g of oil. However, that of oil samples mixed with grape seed and peel extracts are 2.42 and 2.40 mg KOH/g of oil respectively. The same trend was observed for samples at the end of 15, 35 and 50 days. This result confirmed that addition of grape extract to the oil sample reduces the formation of free fatty acid and indirectly rancidity. The result obtained in this work is in agreement with the work of Etti *et al;* (2012). They observed that rancidity is usually accompanied by free fatty acid formation. The value of the free fatty acid was higher in oil sample mixed with grape seed extract than that of oil sample mixed with grape peel extract. This showed that the formation of free fatty acid is slower in the oil sample mixed with grape peel extract than that of sample mixed with grape seed extract. Therefore, extract from grape peel is more effective in reducing oxidation of oil sample than that of grape seed.

pH Value.

The effect of extract on the pH on oil samples for a period of 50 days is showed in Table 5. Samples with extract for the various days show lesser pH value as compared with those of the sample without extract. This indicates that samples with extract are more acidic than sample without extract. The same trend was observed as the samples were subjected to pH analysis for more days. The reduction in pH value signifies lipid oxidation in which the activity of enzymes and microorganisms is greatly inhibited. Sample with seed extract is having little reduction in pH value on comparison with sample with peel extract.

Conclusions.

Antioxidants were extracted from an oven dried grape peel and seed samples using solvent extraction method. The antioxidant potential of grape peel and seed extracts was evaluated based on their ability to preserve a mixture of groundnut seed oil and cow fat from deterioration for a period of 50 days. The Rancimat analyses in term of oxidation stability for the oil mixture without extract, and on addition of grape seed and peel extracts are found to be 67 minutes, 569 minutes and 553 minutes respectively.

The antioxidant effectiveness of the grape peel and seed extracts on the oil sample were within the range of 22.58% to 30% and 16.77% to 29.00% respectively. This clearly showed that grape extracts has an antioxidant potential and capable of preventing lipid oxidation thereby prolonging the shelf life of fat and oil food stuffs. It was observed from the AAS, Rancimat and peroxide value analyses that grape fruit peel extract is more active than seed extract in preventing oxidation of oil mixture. However, in term of free fatty acid and pH values, seed extract was found to be more active as an antioxidant than peel extract.

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